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Henrique de Amorim Almeida · Joel Oliveira Correia Vasco ·
Ricardo de Jesus Gomes · Sandra de Jesus Martins Mourato ·
Vânia Sofia Santos Ribeiro *Editors*

Proceedings of the 2nd International Conference on Water Energy Food and Sustainability (ICoWEFS 2022)

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Preface

The second **International Conference on Water, Energy, Food and Sustainability (ICoWEFS 2022)**, taking place in Portalegre (May 10–12, 2022), Portugal, aims to be a major forum to foster innovation and exchange knowledge in the water-energy-food nexus, embracing the Sustainable Development Goals (SDGs) of the United Nations, bringing together leading academics, researchers and industrial experts. The conference expects to foster networking and collaboration among participants to advance the knowledge and identify major trends in the abovementioned fields.

The world is facing unprecedented challenges to mitigate climate change and adapt to its negative impacts, affecting the global economy and society. Europe intends to take the lead on the transition to sustainability, as a chief priority of Horizon Europe is a European Green Deal to transform Europe in a climate-neutral continent, fostering disruptive innovation and the deployment of new technologies and innovative solutions, helping to create a sustainable future.

Innovation regarding water, energy, agri-food, bio-economy, natural resources and environment will speed up the transition toward sustainability, promoting water and food security in the world.

A climate-neutral continent by 2050 will drive technological, economic and societal transformations toward circular economies and green and clean technologies and the decarbonization of energy-intensive industries.

The conference will be a networking and collaboration among participants to advance the knowledge and identify major trends in the fields mentioned above, even in an online format according to the health rules.

We are grateful to the authors from 16 countries with their contribution of 55 papers accepted to be presented at ICoWEFS 2022 and published by Springer Nature, to the directors and staff of the Polytechnic of Portalegre and the Polytechnic of Leiria for their support, to the research centers and sponsoring companies, to the members of the scientific committee and external reviewers, keynote speakers and, finally, to the members of the organization, who with redoubled efforts during a pandemic time managed to carry out this conference.

We hope that we can meet again at the next ICoWEFS Conference.



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Keynote Speakers

Combating Climate Change with Phytoremediation. Is It Possible?

Ana Luisa Fernando

NOVA School of Science and Technology, Lisbon University, Portugal



Ana Luisa Fernando is Associate Professor at Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal. She is Researcher at MEtRiCS, Mechanical Engineering and Resource Sustainability Center, hosted by Universidade do Minho and Universidade NOVA de Lisboa. She was graduated in Applied Chemistry (UNL), in 1990, with an MSc in Food Technology/Quality (1996, UNL) and a PhD in Environmental Sciences (2005, UNL). She has been working in the field of Food Technology and Safety, by testing natural compounds extracted from plants into biopolymers for food packaging or as additives for food preservation. Parallel to those activities, she has been working with industrial crops for 30 years, with special interest on studies related with the sustainability of industrial crops production and its exploitation as a source of biomass, ecocompounds and ecomaterials for the bio-economy. She has supervised: 7 PhD thesis (concluded), 12 PhD underway, 111 MSc thesis (concluded) and 74 graduation thesis (concluded). She is currently coordinating the ERANETMED project MediOpuntia, and she is also coordinating nationally the H2020 projects GOLD and MAGIC and is Author and Co-author of several publications.

Some Applications in Hydrogen, Renewable Energy and Bioenergy

José Luz Silveira

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José Luz Silveira is graduated in Mechanical Engineering from the Federal University of Itajubá (1986), Mathematics from the Education and Research Foundation of Itajubá Faculty of Philosophy, Sciences and Letters (1985), master's in Mechanical Engineering from the Federal University of Itajubá (1990) and Ph.D. Mechanical Engineering from the Faculty of Mechanical Engineering – UNICAMP (1994). He is Visitante Senior at Federal University of ABC – UFABC, Full Professor at São Paulo University – UNESP, Coordinator of Institute of Bioenergy Research and Head of Laboratory of Optimization of Energy Systems. He has experience in mechanical engineering, focusing on energy, thermodynamics and heat transfer, acting on the following subjects: renewable energy, bioenergy, cogeneration, thermoeconomic analysis, fuel cell, technical, economic and environmental analysis of power systems.

Management of Biomass Parks in Power Generation Plants

Julio Terrados-Cepeda

University of Jaén, Spain



Dr. Julio Terrados-Cepeda holds a Ph.D. in Engineering from the University of Jaén (Spain) since 2005 and master's degrees both in Aeronautical Engineering (Madrid Polytechnics University, 1989) and in Business Administration MBA (IDEOR, 1994). He teaches and researches at University of Jaén since 1994 and serves currently as Tenured Senior Lecturer at Projects Department. He is also External Professor at Universidad Internacional de Andalucía (UNIA), Universidad Internacional de La Rioja (UNIR), and Visiting Professor at Universidad de Cartagena (Colombia).

Dr. Terrados main research interests are focused on strategic planning, sustainable energy planning and renewable resources assessment. He has co-authored thirty-nine peer-reviewed papers and twenty-four books and chapters. He has been also main Researcher or Participant in about twenty research projects funded by public institutions or private companies. He currently leads the research group GIDIES (R&D in Engineering, Energy and Sustainability) at the University of Jaén, which focuses its research on the evaluation of renewable energy resources, the management of smart grids and smart cities, the thermal and electrical use of biomass and energy planning and foresight.

In the academic field, Dr. Terrados has been Vice President for Strategic Planning, Quality and Social Responsibility at University of Jaén, Rector's Delegate for Strategic Planning and Quality at University of Jaén, Vice President for Strategic Planning, Assessment and Social Responsibility at International University of Andalucía (UNIA) and Director of the Engineering Graphics, Design and Projects Department, among other positions.

In the professional area, Dr. Terrados has been Managing Director of the Energy Management Agency of Jaén region, International Programmes Manager at Canava Electronica S.A. and Eurofighter Control Manager at Construcciones Aeronauticas S.A. (Airbus Industries).

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From Extraction to Reparation: American National Security and Territorial Adaptation in the Climate Crisis

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Abstract. We are now witnessing the results of our collective destruction around the world. From centuries of colonialism and industrialization where forests were leveled, marshlands drained, rivers tamed, and oil burned, this global alteration is no longer hidden. Many of the lands bearing the brunt of the effects were the ones leveraged as key extraction zones which accelerated the crisis we face today. This paper argues that USVI (United States Virgin Island) mangrove ecosystems can be a case study for fundamental analysis for restoration and conservation ecology issues for sustainable boosting of local communities. It is argued that under the concept of a “reparation zone” a bridge can be achieved in the gap between environment, human community, and disciplinary separation to work towards a pluralistic approach through a new cultural reparation ecology to better represent, operate, and solve the myriad issues of climate change in the Greater United States. By focusing on American territorial possessions, this paper examines lingering plantation histories and argues for how nature-based solutions can generate a new methodology towards addressing climate threats and socio-cultural injustices.

Keywords: Climate change · Nature based solutions · National security · American studies

1 *Natural Security at Risk*

Over the course of its 245 years, the United States has built itself into a major global superpower (Fig. 1). At the foundation of this superpower lies one critical tool: land. What was once a series of 13 colonies grew and expanded through purposeful means to create a country and empire that now spans over 15,000 km from east to west. For a country that wasn't a major territorial superpower in the 18th century or major military power of the 19th century, the United States relied on a form of nation-building that centered itself on the land. Forests for wood, plains for farming and ranching, mountains to mine, and coasts to fish all converged to form a spirit of potential and opportunity. But this opportunity for endless extraction and cultivation has now been met with a serious cost.



Fig. 1. The growth of the United States from 1803 to 1947.

One key driver of American production and growth was the plantation system. Utilized by European colonial powers through the Americas, Southeast Asia, and Africa, plantations used enslaved labor systems to extract various crops or raw materials to then ship to be processed or sold in the global economy. Today, scholars are reflecting on the plantations system itself and framing it as a critical moment in the Anthropocene’s development. Donna Haraway argues that, “scholars have long understood that the slave plantation system was the model and motor for the carbon-greedy machine-based factory system that is often cited as an inflection point for the Anthropocene” [1]. While central to carbon accumulation we are facing today, the plantations were not the sole responsible operation for the climate crisis but present a concise framework towards understanding the nuances between economic growth, cultural violence, ecological exploitation, and political stability. Michael Murphy and Caitlin Schroering posit that, “the plantation directs out attention to global socioecological inequality, or ‘the ways in which humans, nonhumans, and ecosystems intersect to produce hierarchies – privileges and disadvantages – within and across species and space that ultimately place each at great risk.” [2].

As a result of the plantation mechanic, what the United States once built itself on as a source of nation-building, these lands and its people are now facing the collective results of centuries-long consequences. Moving forward, how the United States re-adapts former plantation landscapes will be a critical test of maintaining a natural security; one that is fair and just (Fig. 2).

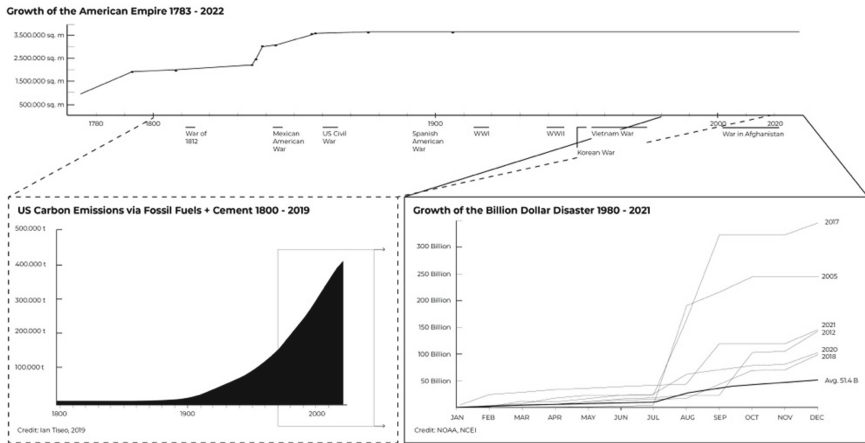


Fig. 2. As the United States grew in geographic size and industrialized, the country began witnessing a substantial increase in billion-dollar disasters starting in the 1980s.

2 Addressing Periphery: The Reparation Zone

Typically framed in the American South, plantations were also utilized in areas outside of the contiguous 48 states. Today, these lands are maintained as territories (Puerto Rico, US Virgin Islands, American Samoa, Guam, Marianna Islands) with the exception of Hawai‘i, which was elevated to statehood in 1959. Within the American conscience, these peripheral lands are often outside daily thought and politically remain outside of policy. Today, the territories lack full congressional representation and only have non-voting representatives in Congress. However, these islands are facing increased rates of hurricanes and typhoons, drought, temperature rise, ocean acidification, and more. As the United States works towards climate adaptation through funding and policies like the Bipartisan Infrastructure Bill (2021) and potentially Build Back Better, there is a unique opportunity for the US to address its territories - its peripheries - and works towards including them in a climate-secure and adaptive future.

Historically, these lands were sites of extraction and experimentation. For outside Colonial and Imperial powers, these were physical spaces to conduct massive experimentation to cultivate and extract the most amount of cash crops as possible. But even more so, these were also spaces to test the limits of enslaved human labor. In the years after the slave plantation system, many of these lands are still dealing with the effects of major land alteration and human exploitation. Stemming from the work of Michael Williams where he offers the concept of the “extraction zone” [3], it is now important to reconfigure this notion.

In a new opportunity to address these chronic issues of climate risk and cultural injustice, the US can tackle territorial and peripheral issues through the concept of a “reparation zone”. The reparation zone would stand as a policy identifier which frames critical spaces to focus re-investment opportunities centered around climate adaptation measures along with funds and programming to address the cultural and social issues that stem from exploitative historical practices. By utilizing this framework, the identified

spaces, lands, communities, or territories become centered and fast-tracked to quickly realize what may normally be trapped in bureaucratic red tape or political stand still. These reparation zones can then primarily focus on implementing nature-based solutions to help tackle the physical threats of climate change, but also how their benefits can help provide jobs, protect cultural heritage, and maintain the human communities that live in the spaces.

As post-plantation American landscapes are found in tropical climates and oceanic geographies, there is a paramount imperative to quickly work towards their adaptation and resilience in the wake of climate change. The US must no longer see these places as extraction zones, but instead catalyze the opportunity to address chronic injustices through climate adaptation and resilience.

3 Mangroves: Socioecological Infrastructure

We all rely on trees, yet for many different reasons. For some, trees provide critically needed shade to cool their sidewalks, others may see trees as a food source. Some see trees as spiritual connectors to the divine realm. Looking to the writing of Rosetta Elkin, she argues that, “as a plant-dependent species, our livelihoods and health are determined by the achievement of plants” [4]. To focus this concept of the reparation zone on one strategy and in one post-plantation landscape, I aim to explore the potential for mangrove restoration in the US Virgin Islands as a form of disaster management and habitat creation.

Mangroves were once a major buffer around the edges of many Caribbean islands. The mangrove forests were the interstitial space between land and water where aquatic fish species used their roots for food and spawning and where birds nested. Culturally, mangrove wood was used for shelters, crafts, and more (Fig. 3) [5]. Today, very few mangroves remain in the Virgin Islands, exposing the shores of the islands and its communities to the threats of sea level rise and storm surge.

The 2017 hurricane season produced two category 5 storms: Hurricanes Irma and Maria. In the two-week period that these storms hit the islands, over 70% of structures of St. Croix were damaged or destroyed. NOAA’s National Center of Environmental Information estimated Hurricanes Irma and Maria produced 167 billion USD in damage across Puerto Rico and the US Virgin Islands [6]. However, by reintroducing mangrove stands and forests into these islands, they can begin to mitigate this damage through storm surge and flooding reduction, helping to protect onshore assets both human and nonhuman.

While ambitious, the abilities of mangroves in climate adaptation are well studied. Zhang et al. found that creating a mangrove stand at 2.5 km in width can reduce storm surge by 50% and an 8 km stand increases the reduction to almost 100% [7] (Fig. 3). By identifying the needed shallow-water habitats for red mangroves to thrive, tactical mass tree planting strategies can be deployed to create a new blue-green infrastructural asset that helps to mitigate increased rates and volatility of hurricanes (Fig. 4). Michael Getzner and Muhammad Shariful Islam found that the average ecosystem value of a hectare of mangrove forest registered at 21,100 USD in 2018 prices [8]. Just one 8 km × 100 m tract with a projection of 100% wave reduction would hold a value of 1.680.000

USD. While the value of these services is complex in nature, the value of mangroves should also aim to include other latent values like cultural value and greater asset and infrastructure protections. As mangrove establishment gets implemented, these latent values must also find ways to transfer back into community development and security

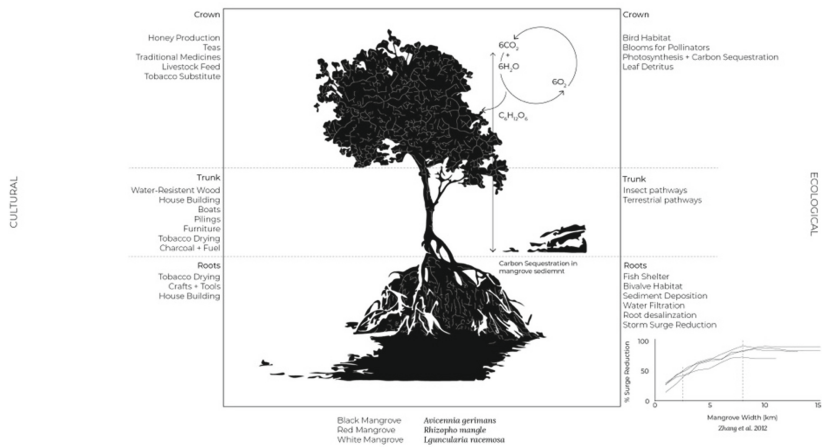


Fig. 3. The mangroves of the Virgin Island and Caribbean at large provide critical ecological services and cultural value.

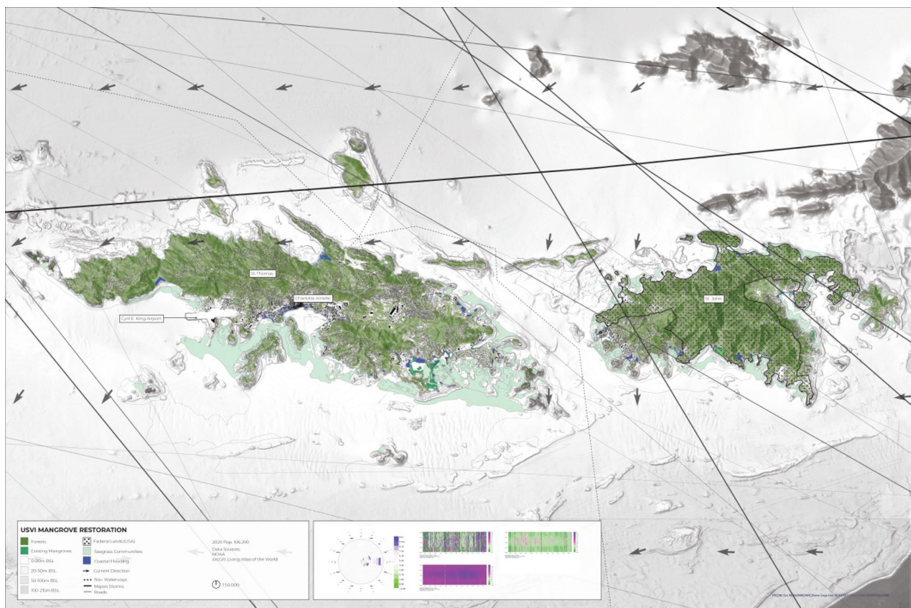


Fig. 4. The Islands of St. Thomas and St. John highlighting seagrass beds as potential new sites for mangrove reforestation.

as well, helping to benefits the residents and communities themselves. In short, the creation of a living land trust through climate adaptation can help additionally provide funds back into local communities to further address needed reparations. Not only will the re-established mangroves act as an almost blue-green wall against the wave power of hurricanes, it will also generate additional habitats for terrestrial and aquatic species that can be leveraged as a green tourist amenity, helping local communities capitalize on this investment even further.

By deeming the USVI as a potential “reparation zone” the US can channel funding and resources into these islands to fast-track climate adaptation and risk aversion. As former plantation landscapes whose land was heavily altered to facilitate crop cultivation and whose labor greatly suffered, re-establishing the lost mangrove buffers can be a potential beginning to a new relationship with the mainland and the federal government. This opportunity is just one measure in a menu of many other options and strategies that can work to engage disparate power structures and disenfranchised peoples and create a new dialogue of co-creation and adaptation for a climate-prepared future (Fig. 5).

4 Periphery Prepared



Fig. 5. Mapping social vulnerability from the Centers for Disease Control and Prevention and the Agency for Toxic Substances and Disease Registry with billion-dollar disasters from 2016–2021.

As the United States works towards a national *natural* security, its territories and peripheral lands must be included in funding opportunities, policymaking, and into implementation. While the climate crisis presents a litany of risks that are perpetually evolving, the US has the opportunity to reconfigure its relationships with its peripheral lands and their peoples to work towards a climate-inclusive and climate-adaptive future (Fig. 5).

By considering the opportunity for a “reparation zone” the US can catalyze its efforts in concentrated areas that are most at risk of climate threats. This framework of understanding will help synthesize ongoing work with necessary funding and processes to quickly address the post-plantation social and ecological issues these lands and its people face each and every day. This work will also offer a chance for the peoples of these islands to be included in the nation-wide endeavor of climate adaptation. As David Immerwahr writes, “at various times, the inhabitants of the US Empire have been shot, shelled, interned, dispossessed, tortured, and experimented on. What they haven’t been, by and large, is seen.” [9].

Nature-Based Solutions, like that of mangrove planting, will be critical to engaging with local communities to ensure that not only are their livelihoods maintained and improved through risk-reduction, but also as an opportunity to allow for the communities that call these lands home to share their knowledge and expertise. Methods of co-creation like this must be implemented throughout the US to utilize a time of immense threat like we are in now as an opportunity to repair chronic socio-cultural issues and injustices. While each party involved may interpret and see a nature-based solution through one particular lens, acknowledging and championing the multiple benefits, uses, and outcomes of a nature-based solution, like tree planting, can also help include more voices and expertise to come together and work towards a deep understanding and application of climate-adaptive and culturally-resilient infrastructure.

Outside of the United States’ efforts of climate adaptation and territorial management is a larger question of countering the effects of the plantation system itself. As Michael Murphy and Caitlin Schroering argue, “ultimately what is at stake here is whether we are able and willing to apprehend the ecological changes wrought by nearly 500 years of the plantation as *not* just a matter of global capitalist expansion and integration, but also racial and colonial assimilation into a world-economic order that institutes a global hierarchy of human and more-than-human life with direct consequence to the Earth system” [2]. This opportunity provides the United States to act as a global leader in the decolonization of former plantation landscapes and creating a new model of adaptation to amplify the people and their land in in the 21st century.

References

1. Haraway, D.: Anthropocene, Capitalocene, Plantationocene, Chthulucene: making Kin. *Environ. Human.* **6**, 1 (2015)
2. Warren, M.M., Schroering, C.: Refiguring the plantationocene: racial capitalism, world-systems analysis, and global socioecological transformation. *J. World-Syst. Res.* **26**(2), 400–415 (2020)
3. Michael, W.: Ebook Central - Academic Complete. *Deforesting the Earth: From Prehistory to Global Crisis: An Abridgment.* University of Chicago Press, Chicago (2006)
4. Elkin, R.: Prefixes of Forestation. *Harvard Design Magazine: Into the Woods*, pp. 6–11 (2018)
5. Bossi, R.H., Cintrón, G.: *Mangroves of the Wider Caribbean: Toward Sustainable Management.* [St. Michael] Caribbean Conservation Association, Barbados (1990)
6. NOAA Billion Dollar Weather and Climate Diasters Homepage (2020). <https://www.ncdc.noaa.gov/billions/>. Accessed 9 March 2022
7. Keqi, Z., et al.: The role of mangroves in attenuating storm surges. *Estuarine Coast. Shelf Sci.* **102–103**, 11–23 (2012)

8. Michael, G., Islam, M.S.: Ecosystem services of mangrove forests: results of a meta-analysis of economic values. *Int. J. Environ. Res. Public Health* **17**(16), 5830–5842 (2020)
9. Immerwahr, D.: *How to Hide an Empire: A History of the Greater United States*. Farrar, Straus and Giroux, New York (2019)



University Staff's Perceptions on Pedagogy in Agricultural Education in East and Southern Africa

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Abstract. In Sub-Saharan Africa (SSA), as in other parts of the world, universities are expected to produce competent professionals and workforce through education. University graduates enhance societal development by utilizing critical thinking and problem-solving skills to develop solutions to environmental and socio-economic sustainability challenges. Yet, higher education in SSA currently fails to provide its graduates the competencies needed for self- and wage employment and in becoming leaders of sustainable societal change.

To identify key areas for higher education quality improvement in SSA, this study investigated university teachers' perceptions on pedagogical knowledge, training and problem-based learning within agricultural programs of eight universities in Kenya, Zambia and Uganda. We distributed web-based survey, with closed-end questions to university staff during October 2020 to March 2021 and received 90 responses. The data was analyzed by calculating distributions and modal values.

Findings show that despite majority of the teaching staff have participated to pedagogical trainings, they do not feel competent on their pedagogical knowledge. Short pedagogical trainings, most commonly participated training types in the study universities, do not facilitate changes in teaching approaches. Teaching staff express keen interests and valuation towards problem-based teaching and learning, yet the actual knowledge and usage of this practice continues to be low. The results indicate that to improve teaching quality and change teaching approaches, pedagogical trainings with adequate length to gain professional teacher competencies, are needed. Pedagogical trainings need to be targeted to the whole teaching staff, but special emphasis should be given to the entry-level teachers and to the universities with currently lowest perceived pedagogical knowledge and training participation.

Keywords: Pedagogy · Higher education · Problem-based learning · Sub-Saharan Africa

1 Introduction

The rapidly changing world, in terms of demography, environment, technology, globalization and trade, poses challenges, yet also opportunities, to sustainable development

and natural resource management [1]. To solve current ecological and societal sustainability issues and grasp arising opportunities, requires competent and innovative workforce [1, 2]. This is especially the case in sub-Saharan Africa (SSA), that currently struggles with low level of tertiary education, low agricultural productivity, food insecurity, youth unemployment and poverty [3].

Higher education and higher education institutes (HEIs) have a crucial societal function on producing human capital, experts that can foster innovation, solve socio-economic and ecological sustainability challenges and contribute on achieving the United Nations' sustainable development goals (SDGs) [4, 5]. Access to quality education and development of competencies and skills relevant for employment and entrepreneurship, as targeted in SDG 4, will eventually contribute to economic growth, development of just and ecologically stable societies, and increased human well-being.

The quantity of higher education provision and graduates within SSA has grown rapidly within the last decades [3, 4, 6]. However, reports and studies show, that the quality of higher education has not grown with the same pace, but on the contrary, the competencies possessed by HEI graduates do not match on the competencies required by employers or for self-employment, leading to high unemployment rates [4, 6].

The low quality of higher education can be associated to inadequate resources and over-crowded classrooms, yet also to inefficient teaching methods and irrelevant curricula that do not match the labor market and societal needs [4, 6]. Higher education in SSA is mostly based on teacher-centered and lecture-form of teaching that rewards on rote-learning and memorization [7]. This maybe the easiest approach for teaching staff that often lack pedagogical qualifications [4]. However, this method leaves few or no space to information application skills and development of meta-cognitive and generic skills, all highly valued and needed competencies in the working-life [4, 8, 9]. To enhance employment of HEI graduates and provide grounds for solving sustainability challenges, the education in SSA must be transformed to provide skills and competencies utilizable and useful in the real-life context [6].

Student-centered teaching methods, such as problem-based learning (PBL), are suggested methods to improve the quality of education and answer the competence needs of working-life and society as a whole [9]. PBL generates competencies by exposing students to real-life problems, for which they need to develop solutions based on acquired information and its application. PBL is associated in development of both content knowledge, and application skills, and also generic skills, such as problem-solving, critical thinking, communication and management skills [8, 10, 11]. PBL approach can provide students both entrepreneurial skills and worker skills enhancing their career prospects and enabling them to become leaders of societal change towards sustainability.

PBL has been applied for decades in many disciplines in the Global North [12], yet the approach has not taken hold in SSA higher education. HEI teachers play a critical role in adopting and implementing teaching approaches, such as PBL, which in turn have direct effect on the students' learning outcomes and competences. Yet, there is a lack of understanding on teachers' perceptions on the pedagogical context. Investigating teachers' perceptions on the current situation is crucial to be able to pinpoint where changes are most critical to enable PBL adoption and implementation, and how to find ways to narrow the mismatch between graduate competencies and work-life needs.

This study focuses on teaching staff's perceptions of eight universities in Kenya, Uganda and Zambia. Within AgriSCALE and PBL-BioAfrica projects¹, an online survey was distributed to university staff, with questions regarding perceptions of pedagogical knowledge, pedagogical training and problem-based learning approach.

2 Materials and Methods

The research is part of AgriSCALE (<https://www.agriscale.net/>) and PBL-BioAfrica projects' (<https://www.pbl-bioafrica.net/>) activities. In the preparation phase of the projects, a feasibility study was conducted for projects' eight African partner universities: Egerton university, Jomo Kenyatta University of Agriculture, South Eastern Kenya University and University of Nairobi in Kenya, The Bishop Stuart University and Gulu University in Uganda, and The University of Zambia and Mulungushi University in Zambia. This article presents findings of the feasibility study.

A structured questionnaire was developed together with AgriSCALE project partner staff from HAMK, Egerton University and Jomo Kenyatta University of Agriculture. A piloting survey was done for eight staff members of HAMK, resulting to rephrasing questions and other grammatical corrections. The final structured online survey consisted of background questions and substance questions on respondents' perceptions on pedagogy and especially on PBL. Substance questions were closed-ended, with either yes/no or ordinal five scale Likert response options.

Research material was collected between October 2020 and March 2021 using anonymous online survey powered by Webropol 3.0 software. We used purposeful sampling to reach university staff within agricultural programs of the AgriSCALE and PBL-BioAfrica projects' eight partner universities. With the help of local project coordinators, we contacted all agricultural staff within the universities with an email invitation and link to the survey.

University staff members participating to the survey were divided into four categories, based on their work position. This research focuses only on university teaching staff. Respondents of this research includes full-time teachers and teachers with double-role on teaching and university management.

As a descriptive variables, we used home universities and length of teaching experience. Before data analysis, we pseudonymized the home universities of each respondent. From one university, we received only three responses, making the data unrepresentative, especially taking into account the large size of that university. Thus, we excluded this university and these responses from the analysis. The remaining universities of respondents are referred as HEI 1-7 in this article. We categorized length of teaching experience into three categories: (1) junior teachers with 1–5 years of teaching experience, (2) mid-career teachers with 6–10 years of experience, and (3) experienced teachers with over 10 years of experience.

To map the availability and length of pedagogical trainings, we categorized participation to trainings as: no participation, training of one day or less, training of two to

¹ AgriSCALE and PBL-BioAfrica projects aim to improve agricultural education within sub-Saharan Africa. Both projects are coordinated by Häme University of Applied Sciences (HAMK) in Finland.

five days and training of 6 days or over. The categorization was designed by the African partner universities, to correspond to the main training types typically offered.

Data was analyzed using Microsoft Excel Version 2102. In accordance with the ordinal scale data analysis, we computed the distribution and mode values for each Likert scale variables.

3 Results and Discussion

3.1 Descriptive Variables

We received total of 90 responses from university teaching staff from the eight universities. After removing one university from the analysis due to small number of responses, we ended up with total of 87 responses from seven universities. The number of responses from each university (Fig. 1) corresponds rather well with the size of the universities, as generally we received more responses from the bigger universities than from the smaller ones. One third of all respondents identified themselves as female and rest as male. The age of respondents varied from age group of 26–30 years to age group over 60 years, and the teaching experience from 1 year to over 30 years.

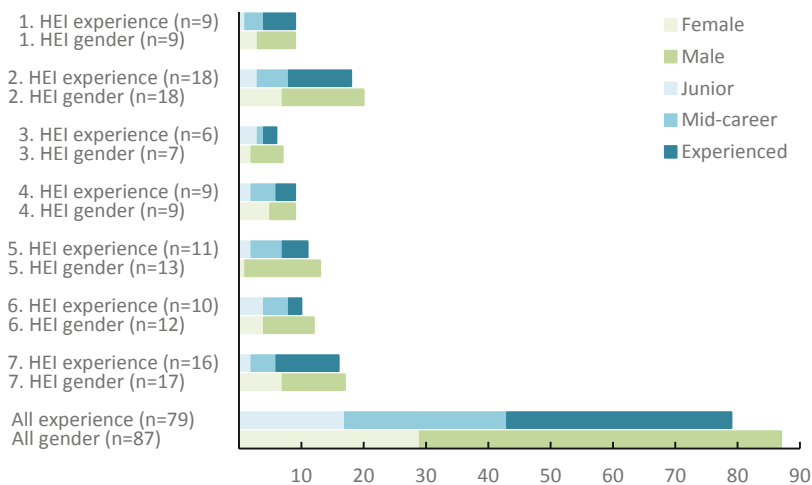


Fig. 1. Amount and distribution of survey responses by home university, teaching experience (junior: 1–5 y, mid-career: 6–10 y, and experienced > 10 y) and gender. Note that the difference between response numbers in relation to experience and gender is due to some respondents not stating their teaching experience, yet all indicated their gender.

3.2 Perception of Knowledge and Interest

Pedagogical theories and PBL approach are generally perceived to be rather poorly known among the teaching staff (Fig. 2). Modes for the perceived knowledge were in

almost all of the cases either 3 (to some extent) or lower (to small extent, not at all). On contrary to expected, the main differences among perceived knowledge were among the different universities and not among junior, mid-career and experienced teachers. Few universities stand out with majority of the respondents knowing constructivist, behaviorism/cognitivism and PBL to only small extent or not at all.

The perceived knowledge of pedagogical theories and PBL as a teaching approach in general is smallest in the junior teachers. This suggest that the pedagogical prerequisites for teaching staff are rather low, or at least do not cover pedagogical theories, leading to low theoretical understanding. This finding is supported by the notion that the study universities do not require pedagogical pre-training from their teaching staff (university representatives, personal communication, October 1st, 2020). Surprisingly, compared to other experience groups, larger share of the most experienced teachers perceive not to know pedagogical theories or PBL at all. Generally, the largest perceived knowledge is among the mid-career teachers. This finding holds even when the few universities stating the lowest knowledge are removed from the analysis. This trend may be caused by the Dunning-Kruger effect: the experienced teachers know enough to understand what they do not know, as the middle-experienced may overestimate their abilities. However, there may also be other factors influencing the perceived knowledge. Pedagogical training methods and topics may have changed during time, leading to different type of competences among the teaching staff, or middle-experienced may have more time or enthusiasm to develop their theoretical understanding.

Constructivist and socio-constructivist learning theories were perceived less know than behaviorism and cognitivism. This perception is in line with the notion that education in most African universities base in so-called "traditional", teacher-centered methods [7], founded on behavioristic and cognitivist learning theories.

PBL approach is perceived to be better known than the theory behind it in each respondent group. This may be due to pedagogy basing more on practices than theories; a practice may be used or studied about without getting acquainted with the theory behind it. The respondents may also have heard about PBL and its basic principles, yet not thoroughly understand the theory behind it.

Interest towards PBL is high among the whole teaching staff, with three fourth or more of the respondents, despite descriptive variable, stated to be interested in PBL to moderate or great extent. The interest towards PBL seem to grow with teaching experience, as well as with perceived knowledge of the approach. The higher the perceived knowledge of PBL, the higher share of respondent were interested on PBL to moderate and great extent. Teaching staff interested on PBL will most probably take opportunities to learn about the practice, or conversely, exposure to the practice, through e.g. training, may arouse the interest towards it.

As the interest towards learning methods in general were not asked, it can't be deduced whether teachers' interest is high specifically towards PBL, or in learning and teaching methods in general. However, the perceived low knowledge on learning theories and PBL, combined with high interest towards PBL indicate clearly that there is a need and demand for learning and thus pedagogical trainings among the whole teaching staff.

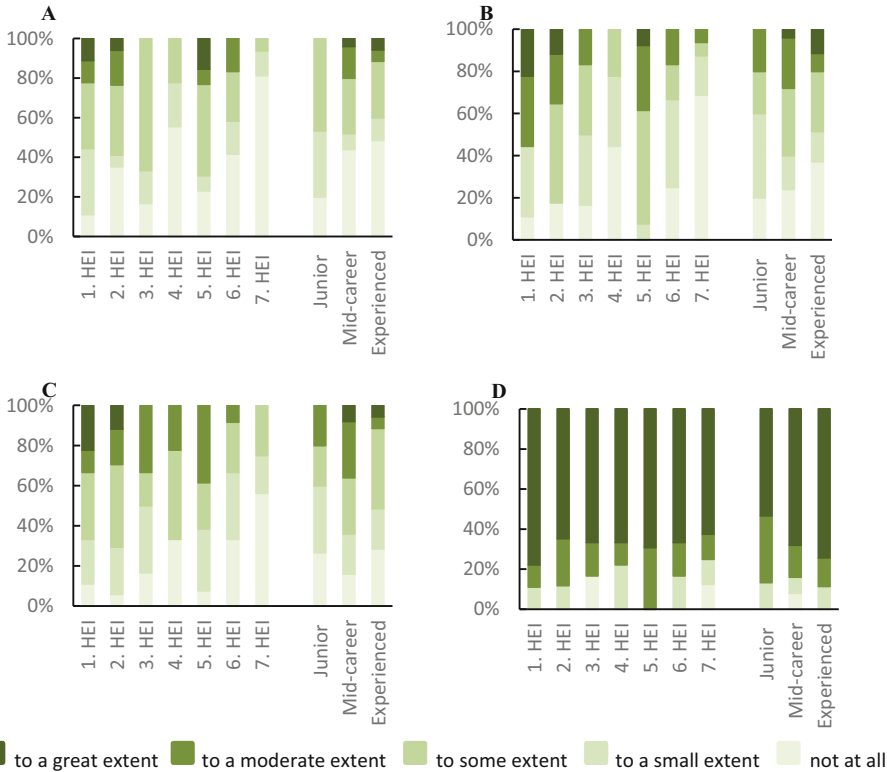


Fig. 2. Perception of knowledge of and interests towards pedagogical theories and approaches among university teaching staff, in relation to different universities (HEI) and to teaching experience (junior, mid-career, experienced). A. Do you know constructivist or socio-constructivist learning theories? B. Do you know any other learning theories such as behaviorism or cognitivism? C. Do you know problem-based-learning pedagogical approach? D. Are you interested in problem-based-learning? Number of responses: 1.HEI, n = 9, 2. HEI, n = 17, 3.HEI, n = 6, 4.HEI, n = 9, 5.HEI, n = 13, 6.HEI, n = 12, 7.HEI, n = 16, junior, n = 15, mid-career n = 25, experienced, n = 35.

3.3 Pedagogical Trainings

Of all respondents, clear majority (76.8%) had participated to pedagogical trainings during their careers. However, there are major differences on pedagogical trainings between different universities, with all respondents from given universities had participated to trainings, and in one university (HEI no 7) 75.0% of respondents have not participated in any pedagogical trainings (Fig. 3). It seems, that the share of teachers participating to trainings are rather equal between the different experience categories. However, when HEI no 7 is removed from the analysis, there is a clear trend showing, that the participation to training as well as the length of trainings grow together with teaching experience. The longer one has been recruited as a teacher, the more opportunities there has been for pedagogical trainings. All in all, most of the trainings participated have been rather

short, lasting for one working week or less. Of all training participants, only 25.8% have participated to pedagogical trainings lasting more than one working week.

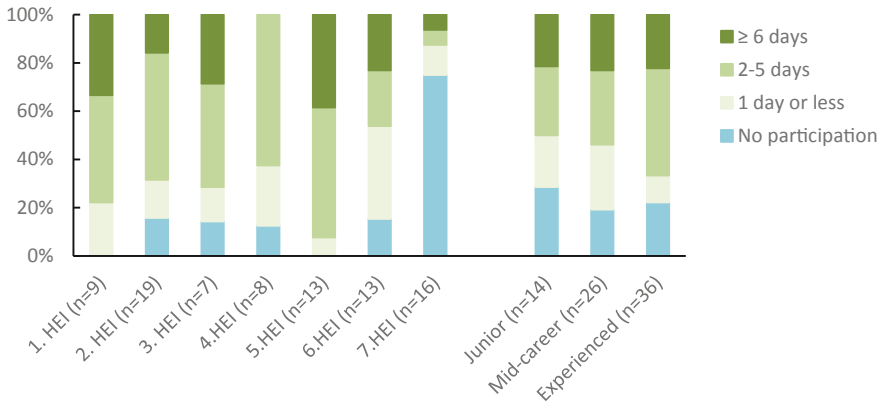


Fig. 3. Participation to training and training lengths, in relation to university and teaching experience.

The length of training participated clearly affect to the teaching approaches (Fig. 4). The longer the training, the bigger share of participants perceived it to change their teaching approaches to moderate or great extent. This indicates that for trainings to have a practical effect on the teaching, longer trainings should be preferred. The trainings also intrinsically affect to the perceived knowledge of pedagogical theories. Respondents from universities with largest share of respondents not participated to trainings and/or generally shortest training lengths also stated the least perceived knowledge on pedagogical theories.

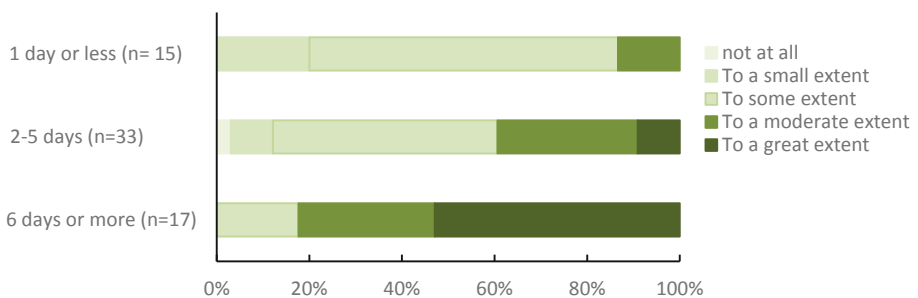


Fig. 4. Length of pedagogical training respondents have participated (y-axis) and the effect training had on changing teaching approach (x-axis), measured as share of responses.

3.4 Perception of PBL

When asked specifically of PBL, 87.2% of all respondents stated to value teaching through real life cases to moderate or great extent, with variation of 75.0–100.0% between teachers of different universities (Fig. 5). The valuation of real-life cases in teaching seem to grow together with teaching experience. However, relatively smaller share of teachers from different universities and teaching experience have used real-life cases in teaching of student groups to moderate or great extent. This repeats the same pattern, as with interest and knowledge about PBL: PBL is more valued than it's actually practiced and the interest towards PBL is higher than the actual knowledge about it. Yet, the notion that almost half of the respondents have used real-life cases in their teaching to moderate or great extent, may suggest that change towards more practical and real-life relevant teaching is under way. However, as the valuation towards other teaching methods is unknown, we cannot conclude whether PBL is valued higher or lower than the traditional, lecture-based teaching methods.

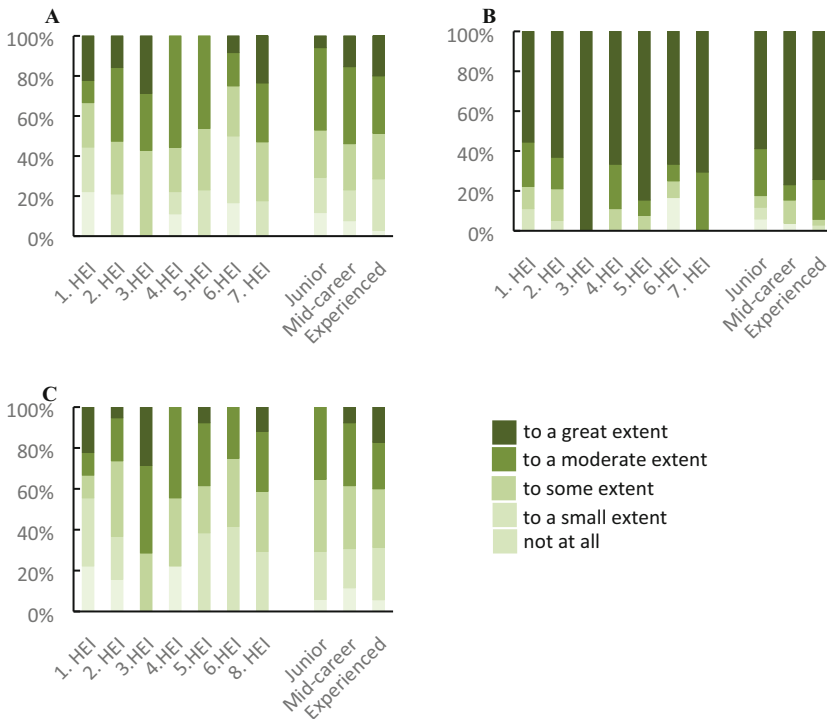


Fig. 5. Shares of university teaching staff's responses to questions: A. have you used real-life cases as topics of student group works? B. Do you see value in teaching through real-life cases? C. Do you have contacts to external partners (such as industry or societal actors) to cooperate in teaching. Number of responses: 1.HEI, n = 9, 2.HEI, n = 19, 3.HEI, n = 7, 4.HEI, n = 9, 5.HEI, n = 13, 6.HEI, n = 3, 7.HEI, n = 17, junior, n = 17, mid-career, n = 26, experienced, n = 35.

External partners are core element of PBL. 37.2% of teachers responded to have external contacts to cooperate in teaching to moderate or great extent. A bit smaller share responded not to have contacts at all or only to small extent. There was some variation between the extent of perceived contacts among teachers from different universities, while the differences between junior, mid-career and experienced teachers are smaller. The answers indicate, that if and when, PBL will be incorporated into the universities' curricula, there already are utilizable contacts to be used in all of the universities, so the whole process would not need to be started from scratch. However, there still is place for further improvement on contacts with external partners.

4 Conclusions

To keep up with the changing world, contribute to societal development and provide employment opportunities to graduating youth, there is a widely acknowledged need to improve the quality of higher education in SSA. Teachers play a major role in this quality shift and thus, it is important to understand how teachers themselves perceive teaching and their own capacities.

Despite majority of teaching staff from the study universities have participated to pedagogical trainings, they recognize lack of pedagogical understanding among themselves, perceiving their theoretical pedagogical knowledge rather weak. Low knowledge rating among the junior teaching staff indicates that the pedagogical pre-requisites for entry level teaching staff are low or non-existent. Perception of knowledge varied between different universities, with respondents from universities with least participation to pedagogical trainings and/or lowest trainings lengths perceived also lowest knowledge. The bulk of pedagogical trainings participated have been short, lasting no more than a working week. These short trainings do not seem to have substantial effect to teaching approaches used, and probably short trainings are also the cause of the low pedagogical knowledge.

Interest and valuation towards PBL are much higher than the actual usage and knowledge of the practice and theory behind it, suggesting that there is a demand to both learn more about the practice and willingness to implement it. This combined with the perceived low knowledge of pedagogy clearly indicates that there is need for more theoretical and practical training for teaching staff. As training length seem to positively impact to changes on teaching approaches, we recommend structured and longer, in-dept trainings to all teaching staff, but especially to the junior staff. To be able to bring PBL to the real-life settings, university teachers should be supported to establish contacts and partnerships to external actors, that can provide workable cases for PBL.

To provide equal opportunities to graduates from different universities, as well as staff members, we suggest especial emphasis on the universities with lowest perceived knowledge and lowest participation to pedagogical trainings. These universities should be supported in developing competent staff and graduates.

For future research, we suggest studies comparing university staff's perceptions on PBL compared to traditional, lecture-based approaches, and inclusion of not only teaching staff but the whole academia including management. There is also need for a study investigating how interest and valuation of PBL can be turned into adoption and implementation, what kind of support would be needed to enable the use of the practice.

References

1. Zubovic, J., Domazet, I., Stosic, I.: Development of human capital as a tool for improving productivity of agricultural sector –case of Serbia. In: 113th EAAE Seminar “The Role of Knowledge, Innovation and Human Capital in Multifunctional Agriculture and Territorial Rural Development, pp. 451–459, Belgrade, Serbia (2009)
2. Hurst, S., et al.: An exploration of the formal agricultural education system in Trinidad and Tobago. *J. Agric. Educ.* **56**(1), 141–154 (2015)
3. The World Bank Group: World Bank Open Data (2022). <https://data.worldbank.org/>. Accessed 8 March 2022
4. McCowan, T.: Quality of higher education in Kenya: addressing the conundrum. *Int. J. Educ. Dev.* **60**, 128–137 (2018)
5. Watson, D., Hollister, R., Stroud, S., Babcock, E.: *The Engaged University: International Perspectives on Civic Engagement*. Taylor & Francis Group, New York (2011)
6. Monga, C., Shimeles, A., Woldemichael, A.: *Creating Decent Jobs: Strategies, Policies and Instruments*. African Development Bank, Abidjan (2019)
7. Muganga, L., Ssenkusu, P.: Teacher-centered vs. student-centered: an examination of student teachers’ perceptions about pedagogical practices at Uganda’s Makerere University. *Cult. Pedagogic. Inq.* **11**(2), 16–40 (2019)
8. Ding, X., et al.: Assessing the effectiveness of problem-based learning of preventive medicine education in China. *Sci. Rep.* **4**(1), 5126 (2014)
9. Easterly, R.G., Warner, A., Myers, B., Lamm, A., Telg, R.: Skills students need in the real world: competencies desired by agricultural and natural resources industry leaders. *J. Agric. Educ.* **58**(4), 225–239 (2017)
10. Abbey, L., Dowsett, E., Sullivan, J.: Use of problem-based learning in the teaching and learning of horticultural production. *J. Agric. Educ. Exten.* **23**(1), 61–78 (2017)
11. Tan, D., Koppi, A., Field, D.: The student perspective in developing graduate attributes through problem-based learning in first year agricultural science. In: *Proceedings of the Australian Conference on Science and Mathematics Education*, pp. 170–175. University of Sydney, Sydney (2014)
12. Servant-Miklos, V., Norman, G., Schmidt, H.: Short intellectual history of problem-based learning. In: Hung, W., Moallem, M., Dabbagh, N. (eds.) *The Wiley Handbook of Problem-Based Learning*, pp. 3–24. Wiley, Incorporated, Hoboken (2019)



Watershed Safety Plan – A New Tool for Water Protection

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Abstract. It is a known fact that an increasing number of areas will face water stress in the future. We have to take even the smallest water sources into use, we have to reuse waters more often and we have to save fresh water as much as possible. This all requires more attention to so-called diffuse pollution as well. We have to reduce water pollution caused not only by big industry and by centralised wastewater services but by every single source/activity no matter how small it is also. This paper describes the differences between point source and diffuse pollution and how the legislation in Finland has developed to remove some diffuse pollution sources into the category of point source pollution. It is most evident that the development will continue when water analyses become more accurate and specific and when we are able to get online data from watersheds due to advanced digital solutions. A new tool called Watershed Safety Plan (WSSP), to eliminate even the smallest diffusion pollution sources, is now under piloting in Finland. The WSSP approach can be seen as a follower to Water Safety Plans and Sanitation Safety Plans implemented by water utilities. The idea is to research watersheds in detail - like using a magnifying glass - to find critical points threatening water quality and to plan actions to get rid of them or diminish risks at least. The WSSP toolbox can be used to reduce risks related to water quantity as well.

Keywords: Water protection · Diffuse pollution · Watershed · Road map for circular economy

1 Water Resources and Diffuse Pollution

Four billion people experience severe water scarcity for at least one month each year. And an estimation is that, by 2025, roughly half of the world's population could be living in areas facing water scarcity [8]. At the same time, water pollution is worrying all around the world. In many countries, even point source pollution is incompletely controlled. The text below is dealing with diffuse pollution, which is the main reason, for example, for eutrophication of many lakes in Finland. Finland is taken as an example because of a new tool called the Watershed Safety Plan (WSSP) approach to fight against diffuse pollution. The WSSP approach is currently piloted in Finland.

1.1 The Need for Diffuse Pollution Control

There are enough water resources in Finland – precipitation is 660 mm/a, and the total amount of water is more than 2000 km³/inhabitant. When talking about water resources, Finland is number one in the European Union [4]. Even so, climate change will bring some challenges to Finland as well. While in many parts of the world severe droughts are worrying, in Nordic Countries, predictions are showing increment in annual precipitation. In Finland, the growing season for vegetation is roughly four months per year only. When the temperature becomes higher, instead of snow cover and frost during winters, the country will face more rain and thus, more diffuse pollution from agricultural areas mainly, but from forests and urban areas as well [10].

So far, the mitigation of diffuse pollution has depended on single actions placed more or less randomly in catchment areas. For example, the agri-environmental programme in Finland has been supporting farmers in implementing sedimentation ponds, wetlands, etc. according to their own interests and naturally on their own farms – without considering the catchments as a whole. This has not been an efficient way of reducing nutrient loads causing eutrophication in waters. Actually, very little or no reduction has been measured [3, 7].

The European Union Water Framework Directive (WFD 2000) has been shown to be the most ambitious piece of EU environmental legislation. Its aim is to restore European waters, but in spite of positive development, not all results have been reached so far. The main objectives were – and still are – non-deterioration of water status and achievement of good status for all EU waters. It seems that some new tools are needed to fulfil the directive’s targets [11].

Implementation of EU’s Drinking Water Directive is to ensure healthy drinking water for all. One important task in this work is the so-called risk assessment, taking into account the entire water production and distribution system. Thus, water utilities producing drinking water should have risks assessed in the catchments as well [2].

There are many other reasons to be listed in supporting the need for new approaches in water protection. One regional document to be mentioned is the Road Map for Circular Economy in Kanta-Häme. Kanta-Häme is a region of 11 municipalities in Southern Finland. The road map which was published in the beginning of 2022 includes five sub-areas, one being water use and water bodies. An ambitious goal under this sub-area is to reach the diffuse-pollution-free region by 2035. One important tool mentioned for working towards this goal is the Watershed Safety Plan (WSSP) approach. Thus, when implemented, the road map is one route to reach the targets of WFD as well [6].

2 The Difference Between Point Source Pollution and Diffuse Pollution

The word *responsibility* has quite an interesting and important role when considering The Constitution of Finland (731/1999) [9]. In Section 20 of the constitution, it is written: “*Nature and its biodiversity, the environment and national heritage are the responsibility of everyone.*” This is underlined in the Environmental Protection Act (86/2000) [1]. In this act, there are several principles that people and organisations should follow in their

daily operations. All should be aware about their effects on the environment, risks should be minimised, the best available technology and best available practices should be taken in use, etc.

Now, when considering the word responsibility and the mentioned legislation, one could answer the following: Who is to mitigate, for example, the pollution seen in the Fig. 1?



Fig. 1. Diffuse pollution originates quite often from a visible point.

Actually, when looking at various pollution sources and legislation carefully, one can notice that the only difference is control. Point source pollution is (or it should be) under control. Small but numerous pollution sources which are not controlled are considered under the concept of diffuse pollution. A good example is on-site sanitation (Fig. 2). Finland enacted new legislation for household-level wastewater treatment in the beginning of this century. Thus, on-site sanitation was taken from the category of diffuse pollution into the category of point source pollution.

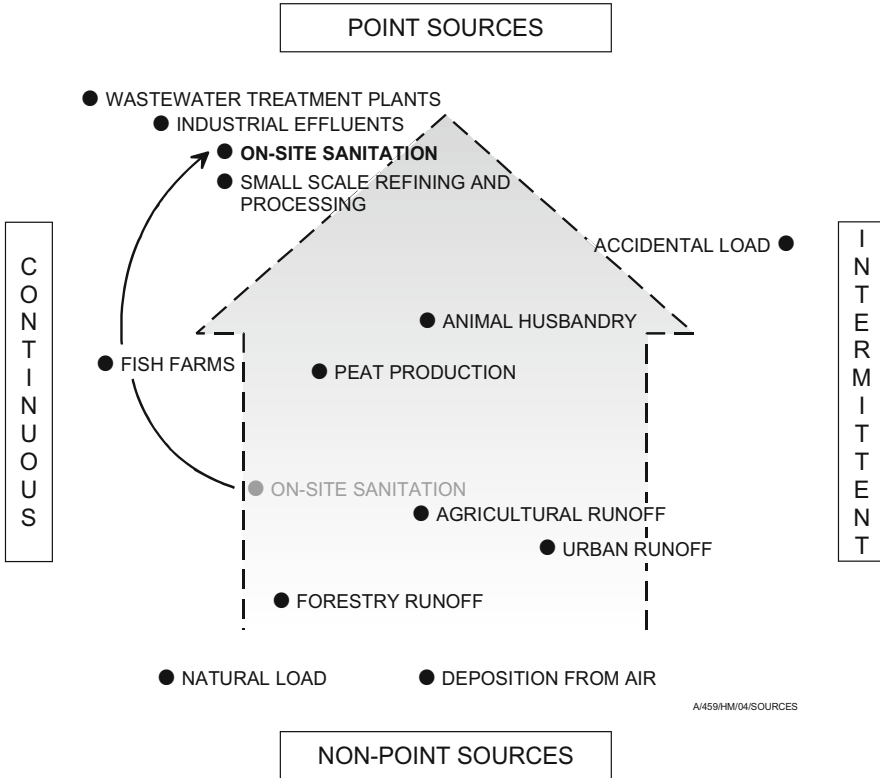


Fig. 2. When legislation and technology are advancing, more diffuse pollution sources will be removed into the category of point source pollution [5].

How can small pollution sources be tackled effectively with existing limited resources? This is the question to which the WSSP approach tries to bring a practical solution. The approach is nothing complicated, only working systematically and using so-called common sense.

3 Watershed Safety Plan Approach

The WSSP approach is now in its piloting phase in Finland. The idea is based on Water Safety Plans (WSP) [12] and Sanitation Safety Plans (SSP) [13] promoted by WHO. WSP and SSP are meant to secure human health by investigating the whole water service chain to find and mitigate all possible risks. WSSP is to do the same in the catchment areas. The only difference is that WSSP is concentrating not only on the human health aspects but also on all kinds of risks – ecological, environmental and even economical risks. By utilising WSSP, together with WSP and SSP, the whole water circle (not the atmospheric water) becomes secured (Fig. 3).

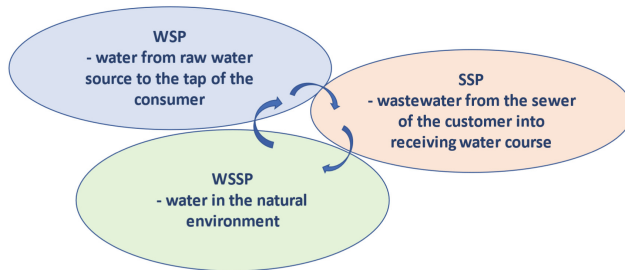


Fig. 3. WSSP approach will complete the safety of water circulation

3.1 How to Implement WSSP

There is no fixed way to utilise the WSSP approach yet. The first-ever piloting is ongoing in Finland in 2021–2022. The pilot is implemented by following the steps of WSP, as shown in Fig. 4.

To ensure that limited human resources are needed as little as possible, all available open data and various GIS-tools are utilised first. After obtaining various maps of the catchment - land use, ditches, networks for wastewater and run-off waters, point source pollution sites, etc. - and researching them one above the other, possible ‘hot spots’ (= points where the probability of diffuse pollution is obvious) can be located. The steps onward depend on the catchment itself. Tools to be utilised are different when working in agricultural areas, forests or in urban catchments. In some cases, the next tool to be considered might be a drone, in some other cases it might be a set of meetings with land owners, and so on. Naturally, when talking about mitigation actions, the variety of tools is really manifold. That is why, instead of WSSP, one should use the concept WSSP

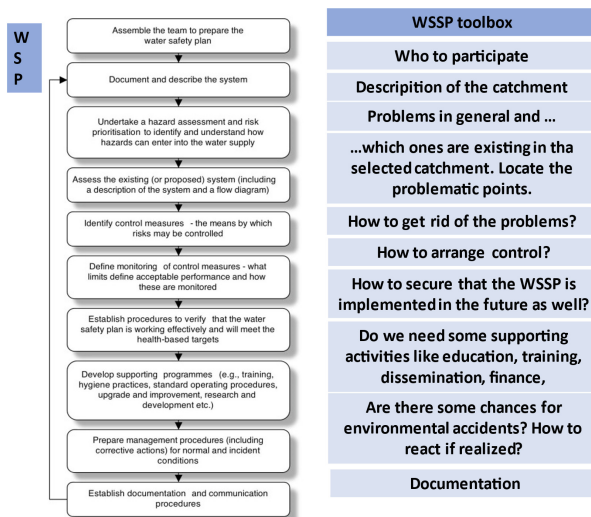


Fig. 4. In the first piloting of the WSSP approach, the steps in WSP are followed to some extent.

toolbox. From the toolbox, the most appropriate tools are to be utilised, and the whole process is tailormade depending on the local circumstances.

So far in the pilot case, the catchment, land use and various networks in the area are defined. An example of the land-use map is in Fig. 5. Today, more detailed investigations are ongoing.

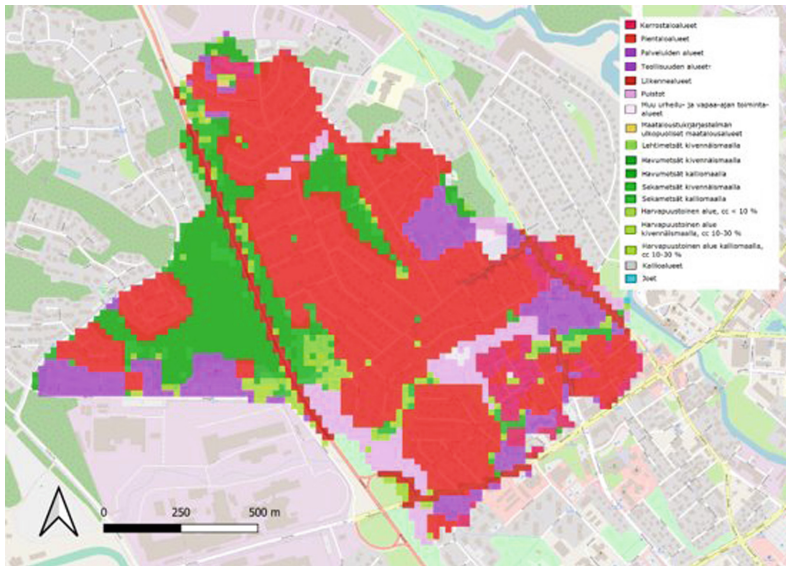


Fig. 5. Various land uses in the Kuhlanoja catchment area in Forssa, Finland

When applying the WSSP approach in another area, one could use much simpler chains of action than given in Fig. 4. There are just a few principles to take into account:

- First use open data and tools which limit the need for human resources.
- In most cases, investigations in private estates are needed. Thus, communication is inevitable to avoid conflicts and drawbacks in water protection.
- Be systematic – it is the only way that all important diffuse pollution sources can be found and sustainable results gained.

3.2 Development of WSSP Approach

It is evident that more of the pollution sources, which today are considered diffuse, are going to be tackled as point source pollution (see the big arrow in Fig. 2). Thus, either the WSSP approach or something similar must be developed. There are several initiatives where the WSSP approach is involved today, and the development work is advancing.

There are many advantages when using the WSSP approach instead of water quality improvements only. For example, flooding in big cities is causing extremely expensive damages, and WSSP could be used in finding the most risky places to cause flooding problems and tools for mitigating those.

4 Conclusions

While there is plenty of work to do to control point source pollution worldwide, in most parts of Europe, the fight against diffuse pollution is at the top of the list. This is seen, for example, from Sect. 1.1. So far, the actions taken have not been very promising. Thus, new, more-efficient tools are required. The WSSP approach is investigating catchments like using a magnifying glass, and even the smallest pollution sources are found and mitigation measures planned, designed, implemented, monitored and reported.




The challenge to create diffuse-pollution-free catchments and regions is really ambitious. The WSSP approach is one of the tools under piloting. More tools are invited to gain experience and make actual progress in water protection work.

References

1. Environmental Protection Act. [en20140527_20190049.pdf \(finlex.fi\)](#). Accessed 20 April 2022
2. Finnish Government, Finland starts implementing EU's new Drinking Water Directive. <https://valtioneuvost.fi/en/-/1271139/finland-starts-implementing-eu-s-new-drinking-water-directive>. Accessed 20 April 2022
3. Holmroos, J., Salmi, P.: Ilmastonmuutoksen monet kasvot Aurajoen ja Paimionjoen vesistökuormituksessa, Aquarius 2020–2021, ISSN 2341-6416, PunaMusta, Helsinki (2020). (Original in Finnish)
4. Kaatra, K.: Finnish water resources, the need and means of saving water, Oral presentation in World Water Day seminar 22nd March 2011, Helsinki (2011). (Original in Finnish)
5. Mattila, H.: Appropriate Management of On-Site Sanitation, Thesis for the degree of Doctor of Technology, Tampere University of Technology, Publication 537, Tampere (2005)
6. Road Map for Circular Economy in Kanta-Häme. [Road Map for Circular Economy in Kanta-Häme \(hamk.fi\)](#). Accessed 20 April 2022
7. Räike, A., Taskinen, A., Knuutila, S.: Nutrient export from Finnish rivers into the Baltic Sea has not decreased despite water protection measures, *Ambio* **49**, 460–474 (2019). <https://doi.org/10.1007/s13280-019-01217-7>. (Springer Nature, Switzerland)
8. Unicef: 2022. [Water scarcity | UNICEF](#). Accessed 19 April 2022
9. The Constitution of Finland. [Ministry of Justice, Finland \(finlex.fi\)](#). Accessed 20 April 2022
10. Veijalainen, N., et al.: Finland's water resources and climate change – Effect and adaption, final report of the WaterAdapt -project, Finnish Environment Institute (SYKE) and Ministry of Agriculture and Forestry, ISBN 978-952-11-4018-1, Edita Prima Ltd, Helsinki (2012). (Original in Finnish, Abstract in English)
11. Voulvoulis, N., Arpon, K.D., Giakoumis, T.: The EU Water Framework Directive: from great expectations to problems with implementation. *Sci. Total Environ.* **575**, 358–366 (2017). <https://doi.org/10.1016/j.scitotenv.2016.09.228>. (Elsevier B.V)
12. WHO/Europe a. [WHO/Europe | Water and sanitation - Water safety plans](#). Accessed 20 April 2022
13. WHO/Europe b. [WHO/Europe | Water and sanitation - Sanitation safety plans](#). Accessed 20 April 2022



Producing Cyanobacteria to Use as Biostimulants

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Abstract. By 2050, the world's population will reach about 10 billion people, which will the need for food by about 60% more than is available today. To meet this need, new processes are emerging to allow more efficient and sustainable intensification of agriculture. In this context, the use of biostimulants has received increasing attention, due to their ability to improve plant quality and yield, stress tolerance, and/or improve the availability of nutrients in the soil. When it comes to Cyanobacteria, the preferred ones are N₂-fixing species, which increase organic nitrogen in the soil, and produce hygroscopic exopolysaccharides, which alter the distribution of water by reducing soil hydrophobicity. Therefore, they decrease soil evaporation and retain moisture, improving soil stability. Wild strains of filamentous N₂ fixing *Nostoc* 135, *Nostoc* 136, *Nostoc* 137, and *Anabaena* 4, provided by Alga2O Lda., were grown in the laboratory with the aim of selecting those that presented the necessary physiological characteristics to be efficiently grown in the laboratory. Therefore, the growth rate, productivity, and exopolysaccharides (EPS) contents were analysed. The EPS obtained from each strain culture (3% g/L) was applied to lettuce seeds (*Lactuca sativa*), to determine the germination rate, primary root length and number of primary leaves produced. As confirmed by other authors, Cyanobacteria are interesting biostimulants regarding germination rates. Other effects to be tested in the future are heat and drought tolerance, water, nutrients, essential oil, and pigment content, all of which are positive aspects that have been previously reported for other *Nostoc* and *Anabaena* species.

Keywords: *Anabaena* sp. · *Nostoc* sp. · Growth rate · Exopolysaccharides · Biostimulant · *Lactuca sativa* · Germination rate · Longest root length

1 Introduction

The exponential growth of the human population raises questions regarding the performance and efficiency of agriculture. Moreover, global arable land is decreasing due to urbanization, degradation and climate change [1]. To address such challenges, several biotechnological approaches have been tried in recent years, namely the use of biostimulants to optimize the productivity of crop plants [2–6]. Biostimulants can be

defined as products that do not contain nutrients and have a beneficial effect on plant growth. Such products consist of humic acids, marine algae (seaweed) extracts, non-hormonal plant metabolites and vitamins [7]. Biostimulants offer a novel approach to the regulation/modification of physiological processes in plants to stimulate growth, to mitigate stress-induced limitations, and, thus, to increase yield in cultivated plants [8]. Among the interesting macroalgal and microalgal species that have been tested as crop biostimulants, cyanobacteria have proved to be among the most interesting.

Many cyanobacteria are known to produce growth promoters such as auxins and gibberellins [9], which regulate plant growth and metabolism of crop plants, thus having a positive effect on seed germination rate and plant growth of vascular plants, namely in rice [10], wheat [11], maize [12], tomato [13], and spinach [14]. Cyanobacteria have also shown interesting antagonistic effects against plant pathogens [15], and increase tolerance to stress conditions [16], among other positive effects. Moreover, cyanobacteria also have positive ecological effects on dry soils, by promoting microbiota [17, 18] and improving soil water distribution, by decreasing evaporation and absorbing condensation moisture, but also by increasing the stability of soil through the ability to withstand erosion, accumulating soil organic matter, favouring the fixation of carbon, producing organic nitrogen, and supplying essential nutrients to plants, thus improving growth, health, and yields of plant crops [15, 17, 19–21]. The most efficient cyanobacteria are N_2 -fixing cyanobacteria, most of which have heterocysts, specialized cells that convert nitrogen into ammonia, making the nitrogen available to plants [22]. Some cyanobacteria also exude exopolysaccharides (EPS) which are hydrophilic and adsorb water and nutrients, thus improving the chemical and physical quality of the soil [17].

The aim of this work was to grow four strains of heterocystic N_2 -fixing EPS producing cyanobacteria, to select those with the required physiological characteristics to be efficiently grown in the laboratory. Therefore, the growth rate, and the content of exopolysaccharides were analyzed, to determine the optimized cultivation parameters for each strain.

The EPS obtained from each strain cultivations, in the form of aqueous extracts, was applied to lettuce seeds (*Lactuca sativa*) to determine the germination index, and thus to conclude the biostimulant effect of these compounds on a model plant.

2 Material and Methods

2.1 Cyanobacteria Cultivation

The cyanobacterial strains *Anabaena* 4, *Nostoc* 135, *Nostoc* 136, and *Nostoc* 137 (Fig. 1), were obtained from the Alga2O Bank, Coimbra (Portugal), on September 10th, 2019, and were transported to the laboratory in test tubes properly covered with foil, to avoid excessive sun exposure. On arrival, cells were transferred to 250 mL flat-bottomed flasks with BG-11 Medium as described in Ripka et al. [23] modified by McFadden & Melkonian [24]. The cyanobacteria were grown in a climatic room (20 ± 2 °C), with constant aeration, under a Daylight cool white fluorescent lamps at $10.8 \mu\text{mol m}^{-2}\text{s}^{-1}$, with a photoperiod set at 16:8 h (Light:Dark).

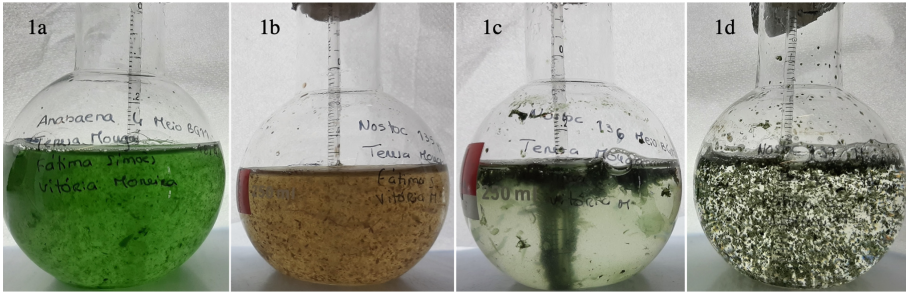


Fig. 1. The four heterocystic EPS producing cyanobacterial strains grown in the assays: 1a) *Anabaena* 4; 1b) *Nostoc* 135; 1c) *Nostoc* 136 and 1d) *Nostoc* 137.

2.2 Cyanobacterial Growth

Each starter culture used a 20% inoculum, which was distributed in 500 mL flasks, as homogeneous as possible. Two replicates were performed, each with 9 flasks, counting from day zero to day 28. Because the cultures are very heterogenous, preventing a uniform sample from being taken, periodically, the total volume of a flask was filtered (Prat Dumas 125 mm, France) and the biomass was dried (Binder FD 115) at 105 °C for 24 h. Dry weight was determined on day zero and every three or four days.

The maximum specific growth rate, μ (g day⁻¹), of each culture were calculated according to Lam et al. [25]:

$$\mu = \frac{\ln x_2 - \ln x_1}{t_2 - t_1} \quad (1)$$

where, x_1 - Initial biomass concentration, x_2 - Final biomass concentration, t_1 - Initial time, t_2 - Final time.

2.3 Exopolysaccharides' Extraction

The extraction followed the methodology described by Flores & Tamagnini [26]. Briefly, 100 mL of culture sample was collected and centrifuged (Eppendorf, 5804) at 14,610 g for 10 min, and the supernatant collected. Dialysis membranes 10 KD (Fisher Scientific, Biodesign™ Cellulose Dialysis Tubing Roll) were previously activated in 70% ethanol for 24 h, washed with distilled water, filled with the supernatant, and sealed. The membranes were placed in a goblet with 2 L of Milli-Q water on a magnetic stirrer plate (Ika, C-Mag HS7) for 24 h, with periodical changes of water. Dialyzed samples were collected and centrifuged (Eppendorf, 5810R) at 18,514 g at 4 °C for 15 min to remove most contaminants. Then, supernatants were collected, and a double volume of cold 96% ethanol was added to precipitate the polymer. The resulting suspension was incubated overnight at 4 °C. For polymer recovery, the suspension was centrifuged at 13,000 g for 25 min at 4 °C. After discarding the supernatant, the pellet was resuspended in a small volume of MilliQ water, freeze-dried and weighed, affording the final EPS content. Results are expressed in mg L⁻¹.

2.4 Germination Assays

The four cyanobacterial EPS were rehydrated with Milli-Q water to a final concentration of 3% and were stored at 4 °C until use. Due to the gelatinous nature of the EPS extracts, they were placed in a 45 °C water bath for 20 min. Three replicates of 15 seeds each were used. The seeds were immersed in 1 mL of extract for 2 h and then placed in a Petri dish with 2 sheets of filter paper previously moistened with Milli-Q water. The Petri dishes were sealed and placed in a climatic chamber (Aralab, Fitoclima D1200PLH) with a 12:12 h photoperiod, temperature at 20°C, and humidity at 90%. The effect of the EPS was evaluated by determining the germination rate (GR, Eq. 2) and the longest root length and number of leaves [27], for 5 days.

$$GR = \frac{\text{number germinated seeds}}{\text{total number of seeds}} \times 100\% \quad (2)$$

2.5 Statistical analysis

All assays were performed in triplicate, except for the growth curves that were performed in duplicate. Data are expressed as mean \pm standard deviation. All statistical analyses were considered significant at p -value < 0.05 . To test normality and variance homogeneity, the Kolmogorov-Smirnov and Shapiro-Wilk tests were used, respectively. As the data did not meet these assumptions, the non-parametric Kruskal-Wallis tests were used. Statistical analyses were performed using IBM SPSS statistical software, version 21.0 (IBM Corporation, Armonk, NY, USA). Calculations were performed with SPSS Statistics 28 (IBM Corporation, Armonk, NY, USA).

3 Results and Discussion

3.1 Cyanobacterial Growth

The four strains show relatively extensive growth, with maximum values of specific growth rate (μ) of 0.432 g (DW) day⁻¹ in *Nostoc* 136, at day 17. *Anabaena* 4, *Nostoc* 135, and *Nostoc* 137 have maximum specific growth rates (μ) of 0.136 g (DW) day⁻¹, 0.267 g (DW) day⁻¹ and 0.298 g (DW) day⁻¹, respectively, at days 14, 11 and 17. The cyanobacteria when cultivated in batch system showed classical shape growth curves (Fig. 2). No extensive lag phase was observed in any of the cultures, as the inoculum originated from a dense starter culture (20%), so the need for adaptation to a new medium was reduced. The growth rate of the inoculum was exponential until day 21 for *Anabaena* 4 and day 18 for *Nostoc* 135, *Nostoc* 136 and *Nostoc* 137, days from which the growth rates decreased.

Anabaena 4 has a lag phase that lasts until day 7, corresponding to the adaptation phase of the cells. The exponential phase then begins and continues until day 21 when the productivity achieved is 30.03 mg L⁻¹ day⁻¹. The growth rate decreases during the stationary phase, which lasted until day 25, then the decline phase is visible (Fig. 2a).

Nostoc 135 and *Nostoc* 136 show very similar growth patterns. The productivity is the highest by day 18, during the exponential phase, reaching 20.77 \pm 4.97 mg L⁻¹ day⁻¹

and $23.26 \pm 4.57 \text{ mg L}^{-1}\text{day}^{-1}$, respectively. The strains never reached the declining phase, achieving the maximum biomass concentration on day 28, with of $0.55 \pm 0.06 \text{ gL}^{-1}$ (DW) and $0.43 \pm 0.32 \text{ gL}^{-1}$ (DW), respectively (Fig. 2b, 2c). Finally, *Nostoc* 137 shows a very heterogenous growth rate among the surveyed days, making it difficult to understand the growth curve. Yet, it seems that the strain reached a narrow stationary phase between day 21 and 25, with the highest productivity on the exponential phase day 18 with $14.29 \pm 0.90 \text{ mgL}^{-1}\text{day}^{-1}$ and the highest biomass concentration on day 25, with $0.47 \pm 0.22 \text{ gL}^{-1}$ (DW), followed by a declining phase with a negative growth phase (Fig. 2d).

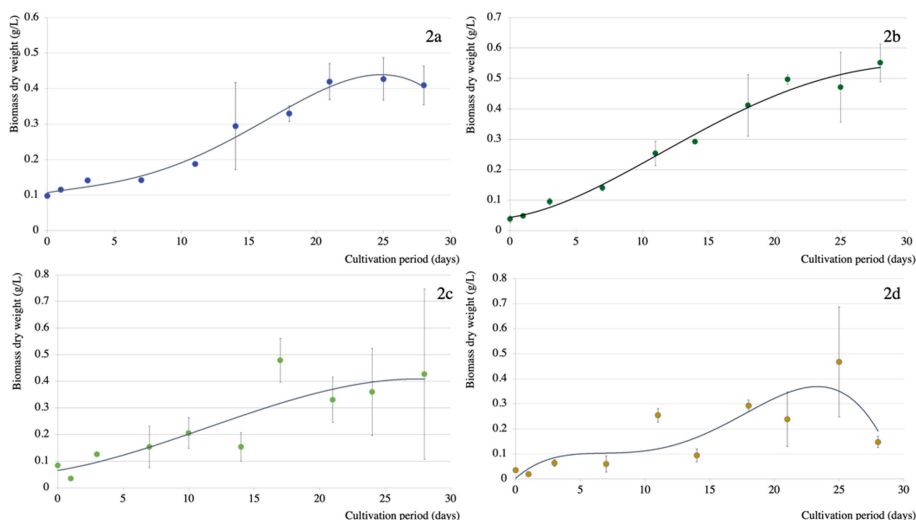


Fig. 2. Growth curves of the 4 cyanobacteria strains grown for 28 days: 2a) *Anabaena* 4; 2b) *Nostoc* 135; 2c) *Nostoc* 136 and 2d) *Nostoc* 137. Data are expressed as mean \pm standard deviation ($n = 2$).

All the strains exhibit a mucilaginous sheath that agglomerates the filaments in the media where they are growing. The most heterogenous is *Nostoc* 136 and the least is *Anabaena* 4. The large standard deviations registered were due to the extremely heterogeneous cultures recorded for these strains.

The growth registered for the strains produced are within the expected values given by other authors [28, 29], although growth may be significantly enhanced by optimizing light and temperature, or supplementing macronutrients [30].

3.2 Exopolysaccharides' Production

The exopolysaccharides extraction yields can be seen in (Table 1). EPS content varies considerably among strains, with *Anabaena* presenting the highest values. Tiwari and co-workers [31] report a range of EPS production for different bacteria between 60 and 1,580 mg L^{-1} . Angelis et al. [32] obtained a content of 1.04 g L^{-1} , for *Arthrospira*

platensis, after 26 days of cultivation. EPS production is associated with the stationary phase [33], therefore, extending the cultivation period beyond 14 days, as in the present work, would probably increase the EPS content of the cyanobacteria.

Table 1. Exopolysaccharide's extraction yield, for the four strains of Cyanobacteria, after 14 days of growth. Data are expressed as mean \pm standard deviation ($n = 3$).

Strain	EPS (mg L ⁻¹)
<i>Anabaena</i> 4	876.50 \pm 91.01
<i>Nostoc</i> 135	195.00 \pm 22.61
<i>Nostoc</i> 136	42.67 \pm 2.87
<i>Nostoc</i> 137	5.67 \pm 0.60

3.3 Biostimulant Assay

Lettuce seed germination was registered daily, for 5 days, and the germination rate was determined. The tested EPS extracts were much efficient than the control, especially on day 1, allowing a germination of more than 70% of the seeds on the first day and more than 93% of the seeds on the second day (Fig. 3). Statistical analysis reveals that there are statistically significant differences ($p < 0.05$) between the germination rate recorded in the presence of all EPS, when compared to the control, by the Kruskal-Wallis tests ($X^2(4) = 25.54$; $p < 0.001$). There are no significant differences among the different extracts.

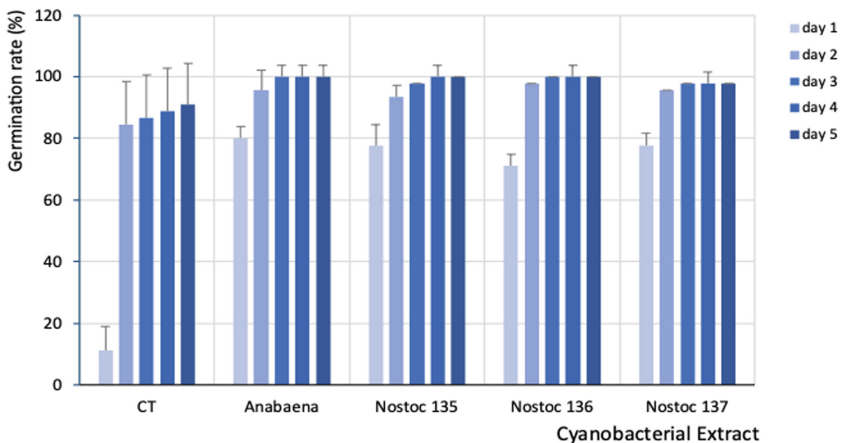


Fig. 3. Germination rates of lettuce seeds, after being soaked in cyanobacterial exopolysaccharides extract. CT (control). Data are expressed as mean \pm standard deviation ($n = 3$).

On the fifth day, the control reached 91% germination, while the EPS extract from *Anabaena*, and *Nostoc* 136 reached 100% on the third day, EPS extract from *Nostoc* 135 reached 100% on the fourth day and EPS extract from *Nostoc* 137 reached 98% of germination rate from the third day on.

As to the length of the longest root after five days of growth, the results are also promising, for the control only reached 0.35 cm by the fifth day, while the EPS extract from all the cyanobacteria tested reached longer lengths (between 1.09 and 1.11 cm). Also, statistical analysis showed the existence of statistically significant differences ($p < 0.05$) between the longest root length measured in seedling in the presence of all EPS, when compared to the control, by the Kruskal-Wallis tests ($X^2(4) = 36.705$; $p < 0.001$). Once again, there are no significant differences among the different extracts in this variable.

Finally, the number of leaves is less impressive, but also noticeable, with the control presenting a mean number of leaves of 1.78, while the lettuces germinated under the cyanobacteria EPS extracts showed a mean number of leaves ranging from 1.85 to 2 (Fig. 4). No significant differences were detected in any of the extracts and the control.

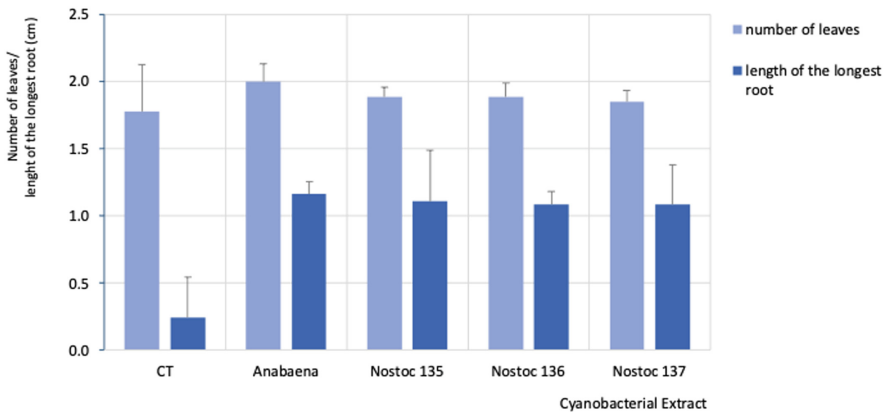


Fig. 4. Number of leaves and length of the longest root, of lettuce seedlings after five days of growth. Data are expressed as mean \pm standard deviation ($n = 3$).

Similar results were obtained by other authors not only for lettuce but also in other crops [22, 34] showing that cyanobacteria present biostimulating compounds with high biotechnological potential, among which are exopolysaccharides. In addition to the effect on germination and growth, EPS are also known to increase salt tolerance on crop plants [35], a feature that deserves to be further investigated.

4 Conclusions

This preliminary work on the four new cultivated strains of cyanobacteria proved that all of them are capable of being cultivated in the laboratory and possibly at pilot/industrial scales. The major constraint will be the great heterogeneity of the medium. Both the

optimisation of the growth promoting factors and those that favour EPS production need to be further investigated. In this work the efficacy of EPS as biostimulant has been clearly demonstrated. EPS should therefore be tested on other crops, and other plant growth parameters should also be evaluated, such as resistance to drought and salt stress, and the production of primary and secondary metabolites.

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References

1. FAO: The Future of Food and Agriculture: Alternative Pathways to 2050. FAO, Rome, Italy (2018). <https://www.fao.org/3/CA1553EN/ca1553en.pdf>
2. Hussein, M.H., Eltanahy, E., Al Bakry, A.F., Elsafty, N., Elshamy, M.M.: Seaweed extracts as prospective plant growth bio-stimulant and salinity stress alleviator for *Vigna sinensis* and *Zea mays*. *J. Appl. Phycol.* **33**, 1273–1291 (2021)
3. Selnes, T., Giesbers, E., van den Burg, S.W.K.: Innovation and collaboration: opportunities for the European seaweed sector in global value chains. *J. Mar. Sci. Eng.* **9**, 693 (2021)
4. Xu, C., Leskovar, D.I.: Effects of *A. nodosum* seaweed extracts on spinach growth, physiology and nutrition value under drought stress. *Sci. Hortic.* **183**, 39–47 (2015)
5. Battacharyya, D., Babgohari, M.Z., Rathor, P., Prithiviraj, B.: Seaweed extracts as biostimulants in horticulture. *Sci. Hortic.* **196**, 39–48 (2015)
6. Halpern, M., et al.: The use of biostimulants for enhancing nutrient uptake. *Adv. Agron.* **130**, 141–174 (2015)
7. Kumar, D., Shivay, Y.S.: Definitional Glossary of Agricultural Terms, vol. 1. K. International Pub. House (2008)
8. Yakhin, O.I., Lubyantsev, A.A., Yakhin, I.A., Brown, P.H.: Biostimulants in plant science: a global perspective. *Front. Plant Sci.* **7** (2017)
9. Hashtroudi, M.S., Ghassempour, A., Riahi, H., Shariatmadari, Z., Khanjiri, M.: Endogenous auxins in plant growth-promoting Cyanobacteria—*Anabaena vaginicola* and *Nostoc calcicola*. *J. Appl. Phycol.* **25**, 379–386 (2013)
10. Nasarudin, N.A., Mohamad, J., Ismail, S., Mispan, M.S.: Effect of Nitrogen, Phosphorus and Potassium (NPK) and bacterial bio-fertilizer on the antioxidant activity and chlorophyll content of aerobic rice. *Molecules* **23** (2018)
11. Nisha, R., Kiran, B., Kaushik, A., Kaushik, C.P.: Bioremediation of salt affected soils using cyanobacteria in terms of physical structure, nutrient status and microbial activity. *Int. J. Environ. Sci. Technol.* **15**(3), 571–580 (2017). <https://doi.org/10.1007/s13762-017-1419-7>
12. Sholkamy, E.N., El-Komy, H., Al-Arfaj, A.A., Abdel-Megeed, A., Mostafa, A.A.: Potential role of *Nostoc muscorum* and *Nostoc rivulare* as biofertilizers for the enhancement of maize growth under different doses of n-fertilizer. *African J. Microbiol. Res.* **6**, 7435–7448 (2012)
13. Mutale-Joan, C., et al.: Screening of microalgae liquid extracts for their bio stimulant properties on plant growth, nutrient uptake and metabolite profile of *Solanum lycopersicum* L. *Sci. Rep.* **10** (2020)
14. Mahmoud, S.A., Abd El-Aty, A.M., Kandil, H., Siam, H.S.: Influence of different algal species application on growth of spinach plant (*Spinacia oleracea* L.) And their role in phytoremediation of heavy metals from polluted soil. *Plant Arch.* **19**, 2275–2281 (2019)

15. Singh, J.S., Kumar, A., Rai, A.N., Singh, D.P.: Cyanobacteria: a precious bio-resource in agriculture, ecosystem, and environmental sustainability. *Front. Microbiol.* **7**, 529 (2016)
16. Rodríguez, A., Stella, A., Storni, M., Zulpa, G., Zaccaro, M.: Effects of cyanobacterial extracellular products and gibberellic acid on salinity tolerance in *Oryza sativa* L. *Saline Syst.* **2**, 7 (2006)
17. D'Acqui, L.P.: Use of indigenous cyanobacteria for sustainable improvement of biogeochemical and physical fertility of marginal soils in semiarid tropics. In: Arora, N.K., Mehnaz, S., Balestrini, R. (eds.) *Bioformulations: for Sustainable Agriculture*, pp. 213–232. Springer, New Delhi (2016). https://doi.org/10.1007/978-81-322-2779-3_12
18. Mugnai, G., et al.: Development of the polysaccharidic matrix in biocrusts induced by a cyanobacterium inoculated in sand microcosms. *Biol. Fertil. Soils* **54**(1), 27–40 (2017). <https://doi.org/10.1007/s00374-017-1234-9>
19. Acea, M.J., Prieto-Fernández, A., Diz-Cid, N.: Cyanobacterial inoculation of heated soils: effect on microorganisms of C and N cycles and on chemical composition in soil surface. *Soil Biol. Biochem.* **35**, 513–524 (2003)
20. Muñoz-Rojas, M., et al.: Effects of indigenous soil cyanobacteria on seed germination and seedling growth of arid species used in restoration. *Plant Soil* **429**(1–2), 91–100 (2018). <https://doi.org/10.1007/s11104-018-3607-8>
21. Maqubela, M.P., Mkeni, P.N.S., Issa, O.M., Pardo, M.T., D'Acqui, L.P.: Nostoc cyanobacterial inoculation in South African agricultural soils enhances soil structure, fertility, and maize growth. *Plant Soil* **315**, 79–92 (2009)
22. Gheda, S.F., Ahmed, D.A.: Improved soil characteristics and wheat germination as influenced by inoculation of *Nostoc kihlmani* and *Anabaena cylindrica*. *Rend. Lincei* **26**, 121–131 (2015)
23. Rippka, E., Deruelles, J., Waterbury, N.B.: Generic assignments, strain histories and properties of pure cultures of cyanobacteria. *J. Gen. Microbiol.* **111**, 1–61 (1979)
24. McFadden, G.I., Melkonian, M.: Use of Hepes buffer for microalgal culture media and fixation for electron microscopy. *Phycologia* **25**, 551–557 (1986)
25. Lam, M.K., et al.: Cultivation of *Chlorella vulgaris* using nutrients source from domestic wastewater for biodiesel production: growth condition and kinetic studies. *Renew. Energy* **103**, 197–207 (2017)
26. Flores, C., Tamagnini, P.: looking outwards: isolation of cyanobacterial released carbohydrate polymers and proteins. *JoVE (Journal Vis. Exp.)* e59590 (2019)
27. Tian, Y., et al.: Responses of seed germination, seedling growth, and seed yield traits to seed pretreatment in maize (*Zea mays* L.). *Sci. World J.* 834630 (2014)
28. Madkour, F.F., Kamil, A.E.W., Nasr, H.S.: Production and nutritive value of *Spirulina platensis* in reduced cost media. *Egypt. J. Aquat. Res.* **38**, 51–57 (2012)
29. El Shafay, S.M., Gaber, A., Alsanie, W.F., Elshobary, M.E.: Influence of nutrient manipulation on growth and biochemical constituent in *anabaena variabilis* and *Nostoc muscorum* to enhance biodiesel production. *Sustain.* **13**, 9081 (2021)
30. Moreno Fernández, J., et al.: Outdoor cultivation of a nitrogen-fixing marine cyanobacterium, *Anabaena* sp. ATCC 33047 production of phycobiliproteins from cyanobacteria view project study of the biosynthetic pathway of carotenoids; improvement of the production of carotenoids and f. *Biomol. Eng.* **20**, 191–197 (2003)
31. Tiwari, O.N., et al.: Characterization and Optimization of Biofloculant Exopolysaccharide Production by Cyanobacteria *Nostoc* sp. BTA97 and *Anabaena* sp. BTA990 in Culture Conditions. *Appl. Biochem. Biotechnol.* **176**, 1950–1963 (2015)

32. Angelis, S., et al.: Co-culture of microalgae, cyanobacteria, and macromycetes for exopolysaccharides production: process preliminary optimization and partial characterization. *Appl. Biochem. Biotechnol.* **167**, 1092–1106 (2012)
33. Delattre, C., Pierre, G., Laroche, C., Michaud, P.: Production, extraction and characterization of microalgal and cyanobacterial exopolysaccharides. *Biotechnol. Adv.* **34**, 1159–1179 (2016)
34. Santini, G., Biondi, N., Rodolfi, L., Tredici, M.R.: Plant biostimulants from cyanobacteria: an emerging strategy to improve yields and sustainability in agriculture. *Plants* **10** (2021)
35. Arora, M., Kaushik, A., Rani, N., Kaushik, C.P.: Effect of cyanobacterial exopolysaccharides on salt stress alleviation and seed germination. *J. Environ. Biol.* **31**, 701–704 (2010)



Transport Development Challenges of Brownfield Investments in the Name of Sustainability

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Abstract. Reconstruction of brownfield sites is part of the EU cohesion policy, a priority area for EU development funding, and a permanent theme for the Committee of the Regions. Redevelopment of brownfield sites is also a solution to ensure sustainable urban sprawl and land management. One of the main advantages of brownfield investments over greenfield investments is, that on the one hand it is not necessary to build the utility infrastructure and road network because it is already built, and on the other hand the development is land-saving, as it is not necessary to declare new undeveloped areas as construction areas. Another advantage can be mentioned: the investment is implemented and the improvement of the environmental conditions, contributing to the appreciation and sustainable development of the settlement. At the same time, the development of brownfields causes challenges during urban planning. On the one hand, an attractive regulatory environment has to be created in the master plans for investors, usually with a high building ratio, but on the other hand, sustainable transport for the area still has to be ensured for the long term. According to our experiences, in order to satisfy the cost-effective investment intention of investors, there is a need to ensure the maximum build-up density of the area, which generates a much higher transport demand than before, which the existing transport infrastructure and services can no longer fulfil, and therefore capacity expansion will be required. However, to ensure sustainable settlement development, the additional traffic demand generated by the brownfield redevelopment must be served following the methodology and criteria of sustainable transport development. Using the experience of a Hungarian case study, the authors present a new brownfield redevelopment model, which can help decision-makers and planners to make the right settlement planning decisions, apply optimal transport planning criteria and methods, and select the adequate, sustainable transport development tools for brownfield investments, during preparation and implementation.

Keywords: Sustainable settlement and transport development · Settlement planning · Master plan · Brownfield development · Sustainable transportation development tools

1 Introduction

1.1 Introduction of the Brownfield Development Areas

At the beginning of the 1990s, the loss of the Comecon markets [1] and the withdrawal of Russian soldiers caused a substantial paradigm shift in the country's economy and settlement development [2]. As a result, factories were bankrupted, left without function, and barracks were emptied after the withdrawal of Soviet troops (*between 1945 and 1990, the Soviet army used at least 342 sites, in at least 108 settlements*) [3].

These areas that have lost their function, called brownfields, like urban wounds, are disfigured in the urban structure. There are almost 6,000 hectares of brownfields in Hungarian cities. Most of these areas are located in an urban environment [4].

1.2 Sustainability Benefits of Brownfield Developments

The different definitions in Europe, the United States, and Asia describe brownfield sites in a similar way as abandoned or underused properties where the actual or suspended presence of hazardous substances, contaminants, or contaminants requires intervention to ensure beneficial reuse. The health and economic hazards of brownfield sites and the challenges and opportunities for their reuse are addressed in the international literature worldwide [5].

Despite the difficulties and high costs of brownfield developments, their social and environmental effects are indisputable. A research team examined and evaluated 200 brownfield real estate investments in the United States. The study found that socio-economic factor (income level), green development, and tax were significantly correlated with brownfield renovation [5].

For this reason, European, national and regional development strategies and programs have been set up in recent years to support such developments.

According to the brownfield redevelopment in the EU-conference report (2019), brownfield redevelopment has to be promoted as a solution to limit urban sprawl, land take, and soil sealing. Inspiring policies, good practices, and EU funds have also been explored for efficient brownfield redevelopment [6].

The planning and investment program for the future growth of Hungary's regions, cities, towns, and rural areas is based on the EU Development Plan of Hungary for 2021–2027. The focus areas of the development plan are included in the so-called Operational Programmes. For example, the main objective of the so-called Land and Settlement Development Operational Program Plus is to improve citizens' quality of life. In addition, it is the goal of the integrated urban development interventions local transport, green and blue infrastructure, ICT, and smart settlement, through the brownfield and municipal energy developments, which also serve sustainability and climate protection purposes [7].

One of the most crucial land use recommendations of the National Development 2030 - National Development and Spatial Development Concept (OFTK) is also the economic and well-thought out use of land [8].

Main areas of intervention:

- rehabilitation of brownfield sites with new functions (community, cultural, green space, etc.),
- rehabilitation of rust zones (e.g., family and climate-friendly), including the renovation and utilization of the building stock.

1.3 Legal Framework

The ‘Building Act LXXVIII of 1997’ consists of planning and protecting the built environment, the essential requirements, means, rights, obligations, and related tasks. The ‘Act LXIV of 2019’ amended the previous one and established basic rules for brownfield sites. The Building Act also requires that, if there is a brownfield area in the administrative territory of the local government, the local government is obliged to define the brownfield in the settlement planning tools (e.g., master plan, land use plan, and zoning plan) and to ensure the possibility of redeveloping the brownfield sites during the planning of the settlement development concept and strategy [9].

Brownfield areas so defined in the local master plan, which includes analysis, recommendations, and proposals for the site’s population, economy, housing, transportation, community facilities, and land use. Currently, the Master Plan defines the construction concept of the brownfield redevelopment.

The zoning plan is part of the master plan, which includes detailed rules on how the brownfield area can be used. The building code of the zoning plan specifies the standards for constructed objects, such as buildings on the brownfield, focusing on the building’s physical features, including characteristics that affect accessibility and safety.

According to the current practice, a brownfield redevelopment project starts with studying the building regulations. Then, it continues with the analysis of the relevant parameters of the settlement planning tools (master plan and zoning plan) and then the review of the installation parameters (building code).

Feasibility studies such as the analysis of urban architecture, environment, and transport are done as second steps. Finally, the building program of the brownfield is developed after the feasibility studies, but it is usually based on the urban architecture feasibility.

2 Case Study

Szechenyi Istvan University (SZE) is at the gate of large-scale development. A Science and Innovation Park will be built on the former Biscuit and Waffle Factory site in Győr as a brownfield development project, which will be one of the eight science and innovation parks planned in Hungary.

The establishment of science parks in several countries plays a major role in the functional change of brownfield sites.

According to the experiences of a Czech study, renewable brownfields are more likely to be found in settlements with higher local development potential, proximity to the regional center and the main road network and high quality of local infrastructure [10].

Technology-oriented businesses have settled in these parks, formerly located in industrial and military areas, typically near university and research bases. It was the first time in Hungary in Budapest that science or technology parks were established in brownfield areas (In-fopark, Graphisoft Park) [11].

The Szechenyi Istvan University owns this 3.6 hectares development area. The development area is within 5 min walking distance from the university campus and 10 min from the city centre. The planned investment is divided into three phases. In the first phase of the investment, a 6000 m² building will be renovated for R&D and education use (pink marking in Fig. 1). In the second and third phases (marked with green and blue), new buildings will be established for enterprises, research organizations, research groups, start-ups, spinoffs. Altogether 47,000 m² net floor area is planned to be constructed.



Fig. 1. The site of the former Biscuit and Waffle Factory and the planned Science Park

2.1 Urban Development Tools

The redevelopment of brownfield sites within urban areas is considered a sustainable land use. The use of a methodological approach to brownfield redevelopment should be based on an assessment of the existing context, the external context of the site and the use of local indicators [12]. The redevelopment of the brownfield of the former biscuit factory for science park was examined in the context of the valid settlement development decisions, such as the ‘Long-Term Settlement Development Concept of the City of Gyor (2014–2030)’ [13], and the ‘Integrated Settlement Development Strategy of the City of Gyor (2014–2020)’ [14]. The existing urban planning tools were analysed as well, in detail: the changes in the process of settlement planning, the current legal environment, the master plan of the City of Gyor [15], and the relevant provision of the local ordinance for the protection of the settlement ‘Building Regulations of Gyor Decree of 39/2021 (XI.30.)’ [16].

2.2 Analysis of Urban Architecture

The urban architecture feasibility study focused on the requirements of the building law according to the brownfield plot, the built environment of the district, and the aspects that influence the installation possibilities [17]. The results of the urban architecture analysis

have been defined the installation plan of the brownfield. The results of the analysis on the urban architecture are assumed in Table 1.

Table 1. Feasibility study: analysis of urban architecture

Analysis of indicators	Conclusions
Plot size	The average plot area in the district 500–1500 m; building plot 3.6 Ha
Built-up density	The average built-up density in the district 20–45%; building plot 60%
Building height	The average building height in the district is 7–7.5 m; ‘Cube building’ 25 m; max. Building height 21 m
Morphology	The construction character surrounding the project area shows a very mixed picture

At the time of the Master plan of 2006, the buildings of the former biscuit factory were still standing, and the zoning plan still considered the use of the plot as a ‘commercial service’ area. However, the area was converted to ‘mixed land use’ in 2010 for better market sales. With this action, the city captured its vision of changing the function of the brownfield area.

The utilization of the original parts of the Biscuit Factory related to the university’s research and development activities was included in the 2006 large-scale development plan only at the level of proposals.

Finally, the Municipal General Assembly approved the current valid master plan in 2013, with the 194/2013. (IX. 27.) decree. This decree sets out the current standard construction rules for the area, such as maximum building ratio 60%; minimum green area ratio 20%; maximum floor area ratio 3.0; maximum building height 21 m.

2.3 Transportation Analysis

The primary purpose of the transportation analysis [18] was to design and determine the traffic needs generated by the planned installation.

Table 2. Feasibility study: transportation analysis

Aspects	Conclusions
Location in urban space	Neighborhood district of the university and the city center, close vicinity of the river Moson-Danube
Modal-split	Expected to be similar to the city’s: 40% private cars, 30% PT, 20% walking, 10% cycling
Transport needs of the inner city	Inner city’s transport needs are reasonably fulfilled

(continued)

Table 2. (continued)

Aspects	Conclusions
Transport needs of the outer city	The site is accessible from outside the city
Existing road network	The transport infrastructure network is appropriate, but there is a shortage of capacity in peak hours
Intersection's capacity	The four roundabouts of the access road are exhausted
New transport investments in the wider environment	Western bypass and the construction of a new bridge are in progress
Travel plans	Not available
Bicycle facilities	The site is connected to the expanded bicycle network
Pedestrian facilities	Sidewalks surround the site, but parking cars often hinder walking
Electric charging, micro-mobility	A charging station is in short distance
Current bus service	The excellent bus network, but the frequency is not sufficient

The results of the transportation analysis are presented in Table 2 and Fig. 2.

Based on traffic counting and forecasting of the examined area, it was concluded that its capacity reserves are currently exhausted, and significant congestion is observed, especially along the main axis. Expanding the Radnoti street for a 2×2 lane road would result in a capacity reserve, but it would involve narrowing or abolishing pedestrian, bicycle, and parking facilities. Nevertheless, the width of the two-lane Jedlik bridge cannot be increased as well.

Furthermore, the traffic flow in the four roundabouts along the main access road is being restricted in peak hours. Implementing turbo roundabouts would increase their capacity 1.5 times, however, the built-up density and the short distance of the junctions do not allow it. Installation of traffic lights would also have insolvable territorial limitations.

2.4 Impact of the Proposed Development on the Transportation

In order to satisfy the generated transportation needs of the Science and Innovation Park, the following measures were proposed (see Table 3).

The impact of the planned measures on the traffic volume is referred on the current traffic volume of the Jedlik bridge, 23000 PCU (personal car unit)/day, which is the highest in the neighbouring road network.

Among the highest transportation-related risks, the current overload of the road network and the future skyrocketing traffic demands of housing investments are the most considerable.

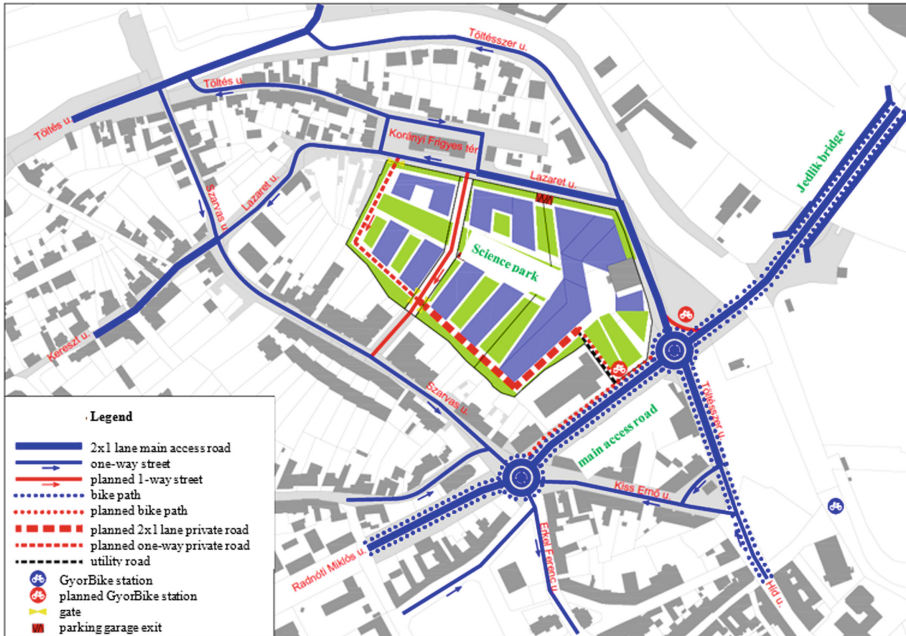


Fig. 2. Road network of the neighbouring area

In the first phase of the project, increasing bus frequency, introducing parking fees in the area, and expanding the public bike system GyorBike will be implemented simultaneously with the renovation of the existing cube building and construction of the inner roads.

Two side roads (Szarvas and Töltésszer streets) are going to be turned into one-way streets according to the proposal in order to mitigate parking needs and support traffic flow. Additionally, bicycle infrastructure is going to be improved locally.

In the second and third phases of the investments, further measures are essential to maintain an appropriate level of service, such as travel plan, work shift (discouraging work start at school start around 8:00 a.m.), and increasing parking fee.

In addition, in the short term, some independent road development projects of the city will have a significant impact on the transportation system of the science park by decreasing the inner traffic volume of the city, such as the development of road No. 83, Western bypass and Ipar Street bridge development.

Additionally, some barely realistic transportation projects for achieving higher road capacity are listed in Table 3. For instance, road development of the Radnoti street with 2×2 lanes, building a new bridge along Jeddlik bridge, reconstructing the four roundabouts into turbo roundabouts or traffic light intersections. A futuristic zip line between the science park and the university and integration of ship transport into public transport would also have an estimated positive impact on the road capacity of the area.

The first phase can be environmentally sustainable by implementing the listed short-term measures. Phases 2 and 3 will be feasible exclusively if more significant transportation developments come true to decrease the traffic volume of the inner city, and a remarkable modal shift will be achieved by implementing sustainable mobility measures. The goal is to minimize the future motorized transport demand of the entire investment.

Generally, it can be stated that the road network's existing and future capacity should be preliminarily taken into account when deciding the building parameters of the brownfields.

Table 3. Transportation development measures and their effect on traffic volume

Measures	Traffic default PCU/day	Estimated impact on motor vehicle traffic, %	Estimated impact on motor vehicle traffic, PCU/day	Estimated impact on road capacity %
Increasing bus frequency	23,000	-5.0%	-1150	
Shuttle bus to university	200	-10.0%	-20	
Shuttle bus to Industrial Park	100	-5.0%	-5	
Travel plan ¹	365	-15.0%	-55	
Work shift ²	23,000	-20.0%	-	
Parking fee	23,000	-2.0%	-460	
Public bike development	23,000	-0.5%	-115	
Road 83. development	23,000	-0.5%	-115	
Western bypass road dev. ³	23,000	-15.0%	-3450	
Ipar street bridge development			-2000	
Road capacity development of the Radnoti str. with 2x2 lanes ⁴				320%
New bridge along Jedlik bridge				320%
Turbo roundabouts ⁵				150%
Traffic light intersections ⁵				200%
Train development	23,000	-1.0%	-230	
Integrate ship transport to PT	23,000	-0.5%	-115	
Zip line between S Park-university	200	-10.0%	-20	
Real estate development	23,000	15.0 %	2500	
Phase 1 additional traffic			365	
Phases 2 and 3 additional traffic			730	

¹ Based on previous Travel Plan experiences [19].

² Calculated based on the average reverse capacity of the intersections within the area of the analysis [18].

³ Based on the macrosimulation traffic model of the planned western bypass road [18].

⁴ Based on the design guidelines of roads [20].

⁵ Based on the estimated capacity of the different intersection types: turboroundabouts and signalized intersections [18].

3 Results

According to the transportation feasibility study's results, it can be concluded that the urban planning tools such as the master plan and the zoning plan, which defines the building code, should not be done without preliminary transportation analyses.

The case study indicated that the brownfield redevelopment areas might cause overbuilding in this current valid legal framework, overloading transportation capacities, thus creating unliveable areas.

The construction rules for a brownfield area, such as maximum building ratio; minimum green area ratio; maximum floor area ratio, maximum building height, should not be defined without the consideration of the transportation circumstances of the area.

The urban architecture feasibility study can help define the installation plan and characteristics of the buildings of the brownfield redevelopment projects but should not be prepared prior to the transportation analysis of the area. The reason behind is that the characteristics of the buildings, the morphology, and the size of the plots cannot determine the brownfield's maximum building ratio sustainably without considering the current and future capacity of transportation infrastructure and mobility services.

During the preparation of a master plan, before defining the building regulations of a brownfield, a transportation impact assessment needs to be executed, which considers the sustainable urban mobility (SUM) principles.

"A Sustainable Urban Mobility Plan is a strategic plan designed to satisfy the mobility needs of people and businesses in cities and their surroundings for a better quality of life. It builds on existing planning practices and considers integration, participation, and evaluation principles." [21]. SUMP also requires a considerable change in the planning principles of cities [22]. While traditional transport planning has focused on providing space for the development of car traffic, SUMP places people and their mobility in the centre: it supports public transport, walking, and cycling and, at the same time, reduce car use.

The planning process is carried out by interdisciplinary planning teams with the involvement of stakeholders. It means that the building concept has to be prepared to understand sustainable urban mobility values in cooperation with interdisciplinary planning teams, such as urban planners, architects, and transportation engineers. The primary purpose of the feasibility studies, both the architecture and the transportation feasibility study, is to ensure the long-term sustainable development of the district and the brownfield.

3.1 Introduction of the New Sustainable Brownfield Development Model

Reconstruction of brownfield sites recently has become the mission of governments, communities, environmentalists, scientists and researchers around the world. Several studies have aimed to sets out a new framework for effective brownfield renovations.

The purpose of some of the studies was, to provide a framework for establishing and optimizing the evaluation for brownfield redevelopment projects [5, 23], or monitor their sustainability [24], however none of them was taking into account the transportation issues.

In order to guarantee the sustainable development of brownfield areas, using the experiences of the case study, a new sustainable brownfield development model has been designed. This new model requires a significant change in the national legal policy framework and calculates with the change of the planning principles of local governments. The new model also summarises the cooperation of the interdisciplinary planning teams and the typical project planning.

The ‘Transportation impact assessment’ has been added as input for the master plan considering transportation aspects as a new process element.

Implementing a SUMP needs to appear earlier in the project evaluation process, following the master plan and the feasibility studies. Previously the SUMP, as the last step, was not able to supply the transportation needs of sustainable transport modes optimally because it did not influence the installation plan.

With this new brownfield development model, the sustainable development of the district is guaranteed, as well as the high-quality environment for citizens and settlers (Fig. 3).

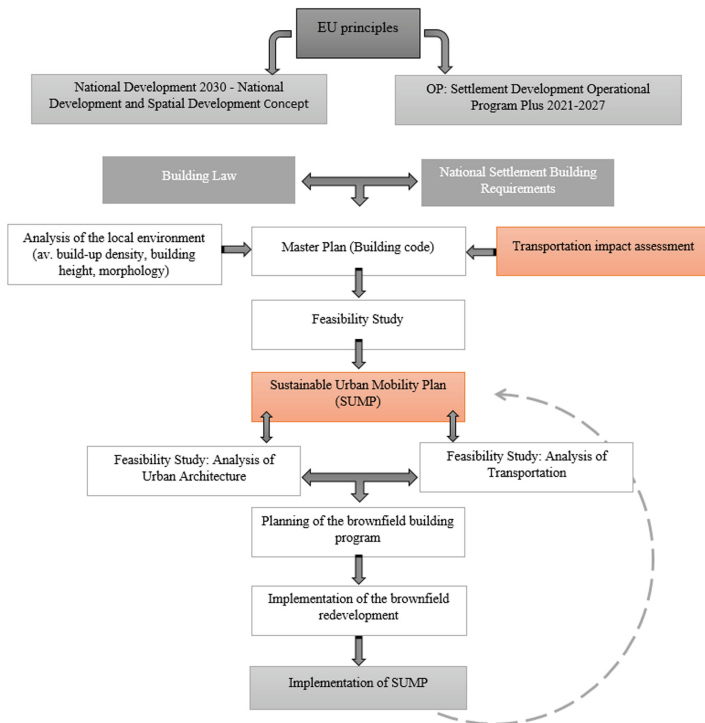


Fig. 3. Sustainable brownfield redevelopment model

4 Conclusions

The rehabilitation and redevelopment of brownfield sites are often less competitive than greenfield sites, especially if their built-up density is economically not optimal for the investors. However, despite brownfield redevelopment's often limited transportation capacity, it has many positive external effects on urban rehabilitation. The European Union funds provide financial support at the international and national levels to implement redevelopment of brownfield sites. However, the rehabilitation can be sustainable unless the transportation aspects are considered during the master planning and if the SUMP appears earlier in the project evaluation process. The proposed model accomplishes the criteria of sustainable settlement and transportation planning additionally ensures the cooperation of the interdisciplinary planning teams and mutual project planning.





References

1. Mosóczy, R., Hajdu, G.: Development of Hungary's Economic Cooperation with the Comecon Countries - Soviet and Eastern European Foreign Trade, vol. 12, no. 4 (Winter, 1976/1977), pp. 3–18 (16) (1975). Published By: Taylor & Francis, Ltd. <https://www.jstor.org/stable/27748471>
2. Magyarország/Hungary, 1989–2009 (ksh.hu)
3. Kádár, K.: The rehabilitation of former Soviet military sites in Hungary - Hungarian Geograph. Bull. **63**(4), 437–456 (2014). <https://doi.org/10.15201/hungeobull.63.4.5>
4. Kukely Gy. – Zábrádi Zs.- Az ipar jelentősége vidéki nagyvárosaink rendszerváltás utáni fejlődésében (elte.hu)
5. Schädler a, S., Morio a, M., Bartke b, S., Rohr-Zänker c, R., Finkel, M.: Designing sustainable and economically attractive brownfield revitalization options using an integrated assessment model J. Environ. Manag. **92**(3), 827–837 (2011)
6. EU Conference report (2019) Brownfield redevelopment in the EU. https://ec.europa.eu/info/sites/default/files/brownfield_conference_report_0.pdf (europa.eu)
7. Ministry of Finance: Land and Settlement Development Operational Program Plus 2021–2027 Terület- és Településfejlesztési Operatív Program Plusz (TOP Plusz) I Szechenyi Terv Plusz (gov.hu) (2021)
8. National Development and Spatial Development Concept 2030 - National Development and Spatial Development Concept (OFTK)
9. Building Law/Étv. - 1997. évi LXXVIII. törvény az épített környezet alakításáról és védelméről - Hatályos Jogszabályok Gyűjteménye (jogtar.hu)
10. Frantal, B., Kunc, J., Nováková, E., Klusacek, P., Martinát, S.: Location Matters! Exploring Brownfields regeneration in a Spatial Contexts (A Case Study of the South Moravian Region, CZ), vol. 21, issue 2 (2013). Moravian Geographical Reports. <https://doi.org/10.2478/mgr-2013-0007>
11. Barta, Gy., Beluszky, P., Czirfusz, M., Győri, R., Kukely Gy.: Rehabilitating the Brownfield Zones of Budapest. Pécs: Centre for Regional Studies, 71. p. Discussion Papers, No. 51 (2006)
12. Cappai, F., Forgues, D., Glaus, M.: A Methodological approach for evaluating brownfield redevelopment project –urban urban science. Open Access J. MDPI Sci. Urban Sci. **3**, 45 (2019). <https://doi.org/10.3390/urbansci3020045>

13. Long-Term Settlement Development Concept of the City of Győr (2014–2030) Megalapozó vizsgálat Győr Megyei Jogú Város Településfejlesztési Konceptiójához és Integrált Településfejlesztési Stratégiájához (2014–2030)
14. Integrated Settlement Development Strategy of the City of Győr (2014–2020). <https://gyor.hu/easy-docs/60c08ca2dba15>
15. Master Plan of the City of Győr _ Győr Megyei Jogú Város rendezési terve (Győr PH - térinformatikai rendszer). <http://195.228.178.212/mapguide/gyor/internet.php>
16. Building Regulations of Győr Decree of 39/2021. (XI.30.) Győr építési szabályzata – GYÉSZ 39/2021. (XI.30.) Önk. rendelet(-ig) módosított 1/2006. (I.25.) Ök. Rendelet. <https://gyor.hu/easy-docs/61a8f546966b1>
17. TSPC Kft: Urban Architecture feasibility study / Megvalósíthatósági Tanlumány- Városépítés (2018)
18. Koren, Cs., Mako, E., Milketics, D., Juhász, M., Winkler, Á.: Transportation Feasibility Study/Megvalósíthatósági Tanlumány- Közlekedés (2018)
19. Szakonyi, P.: The impact of EU funded sustainable transportation development on the quality of life in cities, doctoral thesis (2017). <https://doi.org/10.15477/SZE.MMTDI.2018.003>, <http://phd.szerep.sze.hu:80/?docId=52822>
20. Design guidelines of roads. <https://ume.kozut.hu/dokumentum/278>
21. Rupprecht, S., et al.: Guidelines for Developing and Implementing a Sustainable Urban Mobility Plan, 2nd edn. Rupprecht Consult. Forschung & Beratung GmbH, Weinheim, Germany (2019)
22. Jordová, R., Br ůuhová-Foltýnová, H.: Rise of a new sustainable urban mobility planning paradigm in local governance: does the SUMP make a difference? Sustainability **13**, 5950 (2021). <https://doi.org/10.3390/su13115950>
23. Zhu, Y., Hipel, K.W., Ke, G.Y., Chen, Y.: Establishment and optimization of an evaluation index system for brownfield redevelopment projects: an empirical study. Environ. Model. Software **74**, 173e182 (2015)
24. Padiaditi, K.: Evaluating the sustainability of brownfield redevelopment projects: the redevelopment assessment framework (RAF), land contamination & reclamation. Land Contamin. Reclam. **13**(2) (2005)



Energy Efficiency and Sustainability in an Aquaponic Greenhouse Supported by IoT

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Abstract. The increasing demand for agricultural crops and the necessity to reduce environmental impacts from traditional agriculture have led to the emergence of sustainable production systems such as hydroponics and aquaponics. These soil and pesticide-free systems require less water and fertilizers but need electrical energy and controlled greenhouse environmental conditions to be highly productive. This work presents a monitoring and management system for environmental parameters inside an aquaponic greenhouse, that allows the manager to assess in real-time the working status of the aquaponic system, helping in the detection of critical conditions that require a quick decision. This system was developed to measure, through IoT sensors network, the temperature and the relative humidity of the air, the temperature, pH and the electrical conductivity of the water that contains the dissolved nutrients that feed the growth of the plants. It is possible to visualize the measured parameters via the Internet, on a dashboard, in a mobile application and store these variables in a database. To further increase the sustainability of the aquaponic greenhouse, the electricity consumed during its activity will be produced locally by photovoltaic technology. The technologies proposed in this work may promote the emergence of small models of greenhouses, implemented by communities and populations, reducing production energy costs and transportation resources.

Keywords: Greenhouse · Sensors · IoT · Monitoring · Visualization · Local energy production

1 Introduction

Nowadays the water-energy-food nexus embraces the Sustainable Development Goals (SDGs) of the United Nations to satisfy the constant food production [1].

The economic viability of agricultural crops produced in protected environments, such as greenhouses, is highly dependent on the associated energy and environmental costs.

With this purpose, the monitoring of these variables, as well as the definition of solutions aim at minimizing production costs, which is fundamental for the survival and competitiveness of these companies.

In this context, a new model for collecting physical variables, using a network of sensors and rapid processing of this data, allowing the manager of these greenhouses to make quick decisions to increase the overall efficiency of these production systems is presented below.

1.1 Objectives and Case Study Features

The main objective of this work was initially to analyze the energy consumption of a case study, a 150 m² plant production greenhouse with aquaponic technology, located at Campus 2 of the Polytechnic of Leiria, Portugal, and to develop technological solutions to improve the energy efficiency and the overall sustainability of this activity.

Thus, the present study aimed to design an energy production system by photovoltaic technology, based on a self-consumption scenario or an isolated grid scenario in accordance with current legislation in Portugal. Moreover, the study also aimed to develop an IoT-based monitoring system, using the installation of sensors and program design, so that it is possible to obtain information on key parameters in real-time, which is fundamental in decision-making in case of detection of critical conditions associated

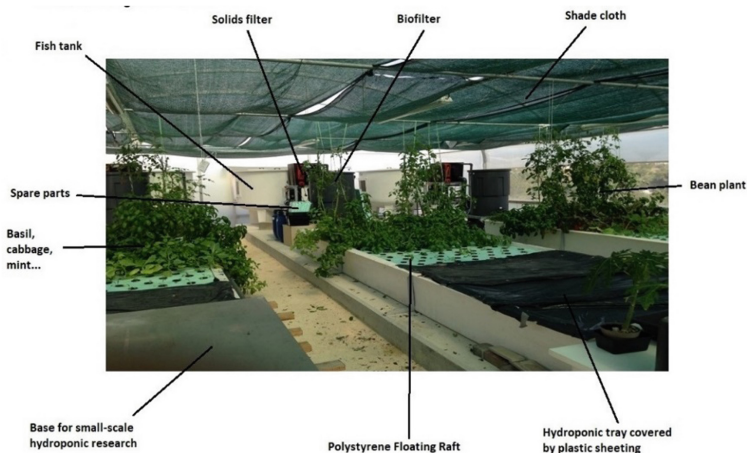


Fig. 1. Main components in the aquaponic greenhouse.

with the nutrient solution and/or climatic conditions of the greenhouse of the case study (see Fig. 1), which has some main components.

The greenhouse features two lateral non-automatic windows for passive ventilation and a precarious indoor shading system, denoting a great room for improvement to adequately deal with summer overheating and winter low temperatures that can delay the growth of fruits and pods. Another aspect will be to introduce systems that detect the state of maturation of the plants and automatic harvesting of fruits and pods, in this intensive production process. But this will be the subject of research and implementation soon.

1.2 Sustainable Production of Edible Plants

Some more exclusive food crops, for certain restaurants or food stores, can use small-scale greenhouses, where the typology of technology developed and presented below will be an option for sustainability and decarbonization of the economy. In this context the edible flowers like dahlia and rose can be used as a source of phenolic compounds with bioactive potential and can be incorporated in human diet [2].

The production of edible flowers in photovoltaic greenhouses can be a sustainable possibility. Not only the productions' methods can be optimized (ex. the microclimate created can reduce pests), but it also makes possible to generate electricity (as was demonstrated in a tomatoes' experimental greenhouse covered with flexible photovoltaic panels) [3–5]. The search for different sources of nutrients (*e.g.* flowers) to be incorporated in human diet combined with best sustainable production practices, using advanced technologies, can provide huge opportunities to improve, not only the productivity, but also the final product quality.

2 Technologies and Developed Model

2.1 Details of This Technologies

For the control and monitoring of an aquaponic/hydroponic greenhouse [6, 7], the objective is to obtain a system in which key parameters such as air and water temperature, relative air humidity, pH and electrical conductivity of the nutrient solution can be observed remotely, either through of a Web page or through a mobile application. It is also intended to be possible to control these parameters to desired values, by using appropriate actuators. These technologies use sensors to obtain parameter values; there are several types of sensors that can be used successfully. The values that are read from these sensors will be sent to a microcontroller. Eventually, this device processes the data and controls the greenhouse using a control unit. The control unit, *i.e.*, a set of actuators that guarantee the control of the parameters, act when, for example, the temperature is outside the defined limits, by activating a fan or other mechanism in order to lower the temperature in the greenhouse.

The microcontroller has the final objective of sending the values of the parameters, so that they can be monitored through a Web page or a mobile application. The type of monitoring and control differs for different existing systems, and normally through

monitoring, it is possible to change the limits defined for this data remotely and in real time. By controlling the parameters, the use of the devices allows enhances the efficiency, since it is not necessary, they are on more time than essential. Figure 2 illustrates what has just been presented [8].

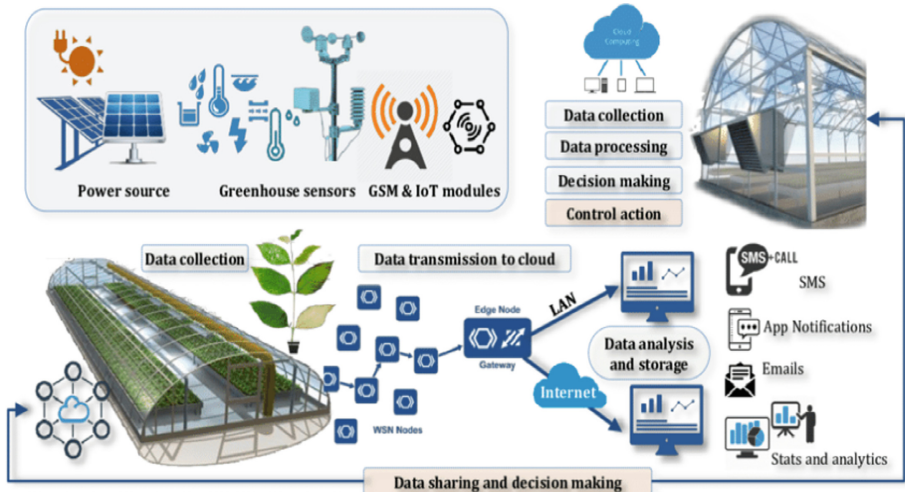


Fig. 2. Greenhouse and associated data control parameters of physical variables.

2.2 Features of Developed Model

Applying the technology presented in Fig. 2, a model was designed for the case study herein presented, consisting in two main areas (see Fig. 3): 1) Monitoring and visualization system of the key physical variables of the greenhouse; 2) Local production of electricity by photovoltaic technology by two production regimes in accordance with national legislation [9].

3 Methodology, Prototype and Results

Considering the components of the model developed for the case study depicted in Fig. 3, this paragraph describes the steps in the design of an electric energy production system, using photovoltaic technology, under two operating scenarios:

- 1) Self-consumption.
- 2) Isolated grid.

A monitoring and a visualization system will, also, be presented with the objective of monitoring parameters related to the plant growth process in the greenhouse and providing its remote viewing via the Internet or mobile application.

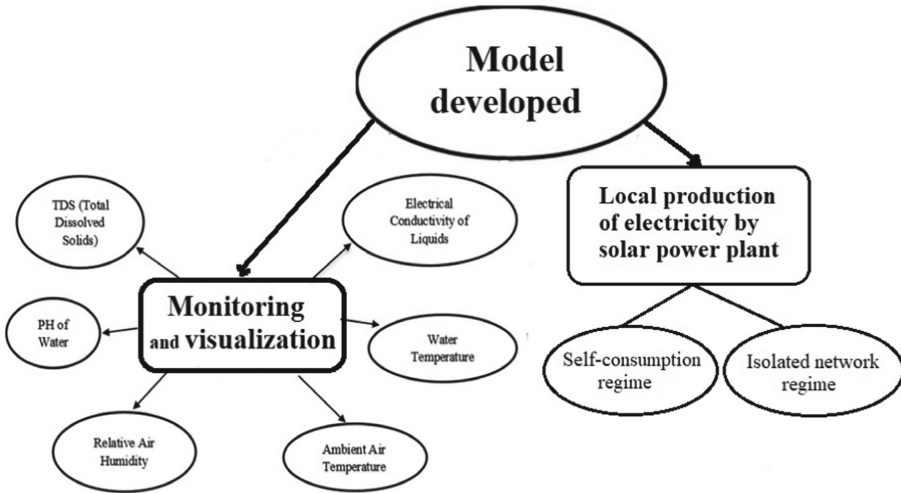


Fig. 3. Model developed in the case study with the power source energy production, telemetry, IoT sensor network, remote monitoring, visualization, and control capabilities.

3.1 General Consumptions

Following an energy audit methodology in accordance with the Portuguese law n° 68-A/2015, which regulates energy efficiency matters and results from the transposition of Directive n° 2012/27/EU of the European Parliament, it was installed one energy analyser equipment in the electric panel of the greenhouse to collect consumption data, during a period of 2-weeks in February 2020, to carry out an analysis consumption of the installation in this season of the year.

After this, a load diagram was created (see Fig. 4) to observe the differences between the consumption of previously existing data as well as the profile of the periods of minimum and maximum consumption, which reached a value of 1.8 kWelectric. This maximum consumption is essential for the design the local electricity production by solar power plant presented in Fig. 3.

3.2 Monitoring and Visualization System

Monitoring and visualization system consisted in the use of telemetry processes, IoT sensor network, monitoring and remote visualization in the control of the equipment inherent to these methods of managing these variables. So, the board ESP32-DevKitC is a small-sized ESP32-based development board produced. Most of the I/O pins are led out to the pin headers on both sides for easy interfacing. Developers can connect these pins to peripherals/sensors as needed. Standard headers also make development easy and convenient when using a breadboard.

This module ESP32-SOLO-1 is a powerful, generic Wi-Fi + Bluetooth + Bluetooth LE MCU module that targets a wide variety of applications, ranging from low-power sensor networks to the most demanding tasks, such as voice encoding, music streaming and MP3 decoding. It has a supply voltage of 3.3/5V DC. Through this microcontroller,

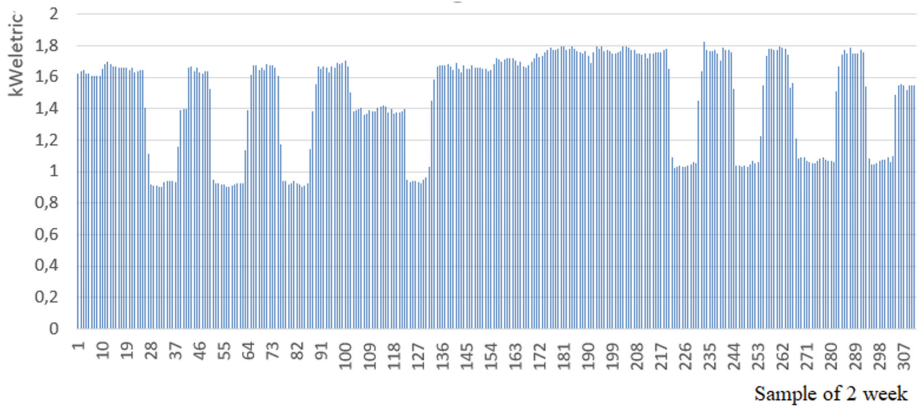


Fig. 4. Load diagram of 2-week sample in 2020 February.

data from the installed sensors is acquired and this information is processed in such a way that errors are minimized.

The Raspberry Pi 4 Microcomputer or Small Single Board Computer (SBC) is like a computer built on a single circuit board, with microprocessor(s), memory, input/output (I/O) and other features required of a fully functional computer. It has a supply voltage of 5V DC and its purpose is to develop the graphical interface.

Sensor values, Table 1, are sent to the Raspberry Pi via the MQTT (Message Queue Telemetry Transport) protocol. MQTT is a communication protocol with low bandwidth and hardware requirements. The broker is installed on the Raspberry Pi, which consists of using the publish/subscribe paradigm to exchange messages. The broker is responsible for receiving and sending messages from publishers to subscribers [10].

Table 1. Components used in the project - prototype designed.

Type	Description/Model/Manufacturer
Sensor	Water Temperature/DHT11/Flux Workshop
Sensor	Environment temperature and relative humidity/DS18B20/ElectroFun
Sensor	pH/ SEN0169-V2/DFRobot
Sensor	TDS e EC/SEN0244/DFRobot
Microcontroller	ESP32 NodeMCU/ESP32 DEVKITC-S1/Espressif Systems
Microcomputer	Raspberry pi 4/ MODEL B/Raspberry Pi Foundation

For this, a MQTT routine/function was created that connects the ESP32 to the Raspberry Pi, as can be seen in Fig. 5. When the MQTT connection is lost, there is a routine that reconnects. The same happens with Wi-Fi.

```
void conectarMqtt() {  
    Serial.println("Conectar MQTT...");  
    mqttClient.connect();  
  
}
```

Fig. 5. MQTT Function [11].

The sensor data/values are sent at the end of each function; see the type of format (Fig. 6).

```
uint16_t IdPub1 = mqttClient.publish(sensor_temperatura, 1, true, String(temperatura).c_str());  
Serial.println("temperatura enviada");  
uint16_t IdPub2 = mqttClient.publish(sensor_humidade, 1, true, String(humidade).c_str());  
Serial.println("Humidade enviada");  
uint16_t IdPub3 = mqttClient.publish(sensor_temperatura_agua, 1, true, String(temperatura_agua).c_str());  
Serial.println("Temperatura da água enviada");  
uint16_t IdPub4 = mqttClient.publish(sensor_tds, 1, true, String(valortds).c_str());  
Serial.println("Nível de Tds enviado");  
uint16_t IdPub5 = mqttClient.publish(sensor_ec, 1, true, String(ec).c_str());  
Serial.println("Nível de EC enviado");  
uint16_t IdPub6 = mqttClient.publish(sensor_ph, 1, true, String(valorph).c_str());  
Serial.println("Nível pH enviado");
```

Fig. 6. Some details of the program for sending data of environment temperature, humidity, water temperature, TDS, pH and EC - electroconductivity through the MQTT protocol.

The block diagram of Fig. 7 presents the processes developed for monitoring and visualization. The ESP32 NodeMCU receives the parameter data from the sensors, where the data is processed and sent via Wi-fi to the Raspberry Pi microcomputer. The data

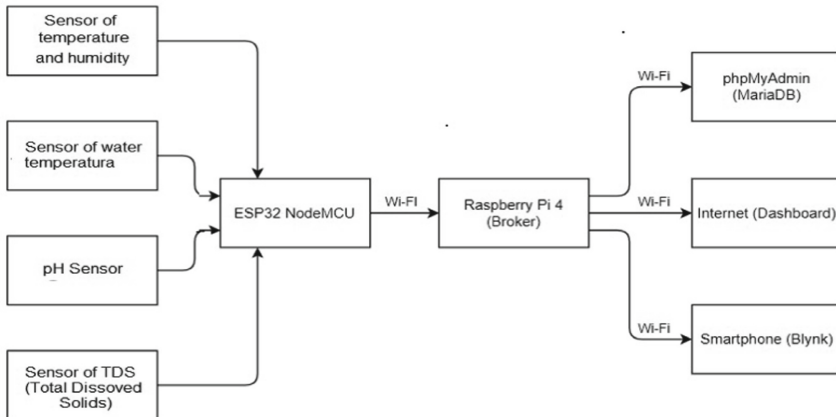


Fig. 7. Block diagram of the monitoring and visualization system

is saved to have a history of the parameters. Data can also be viewed remotely via a computer dashboard or mobile application on a smartphone.

A graphical interface was developed using Node-RED [12], allowing connection with other devices. This interface consists of a dashboard, a Blynk mobile application [13] and a MariaDB database [14]. Node-RED is a flows-based development tool for connecting between devices as part of the Internet of Things - IOT.

To visualize the values of the sensor readings, a panel was created with the monitoring of each sensor. For this it was necessary to develop a flow for each sensor. The graphical interface on the smartphone can be customized the way one want to visualize the values of the devices. It can be visualized through a graph, a text box or a pressure gauge; being this, a simple graphical interface of configuration and very flexible.

To store the values of the sensor readings, a database was created using the MariaDB software. It is a database that was developed by the creators of MySQL and was created from MySQL.

To program the ESP32 NodeMCU, the Arduino software, the Arduino IDE [15] was used. The acquisition of sensor data is done through the software and the same is for sending the data to the Raspberry Pi. To carry out these processes, libraries such as WiFi, DHT, OneWire and DFRobot_PH were used. The DHT11 sensor has the objective of acquiring the ambient and relative temperature data. In order the reading of the environment temperature values to be the most correct, an arithmetic average was calculated from the five readings received from the sensor.

3.3 Electricity Local Production of Self-consumption Regime

In this article, only an explanation of the local energy production component in the self-production regime will be presented. The result of the software - PVsyst V.6.81 simulation shows that the photovoltaic system has an energy production of 5.530 kWh/year, with a performance index of 83.16%.

The solar fraction of the system is 30.21%, that is, close to 30% of the energy that powers the greenhouse comes from the photovoltaic system, with the rest being purchased from the grid.

Through the graph of Fig. 8 it is possible to observe the useful energy produced by the system over the months, the system losses from the inverter and the losses of the photovoltaic group.

With this scenario of electricity production, it is possible to reduce the purchase of energy from the national grid and the surplus energy produced by the panels can be injected and sold to the national grid. The investment for the photovoltaic system will be around 7.000 EUR for around 16m² of photovoltaic panels. Since through this self-consumption system it is not possible to have a very high energy production by this technology (30%), the loads of the stoves are loads that are in continuous operation.

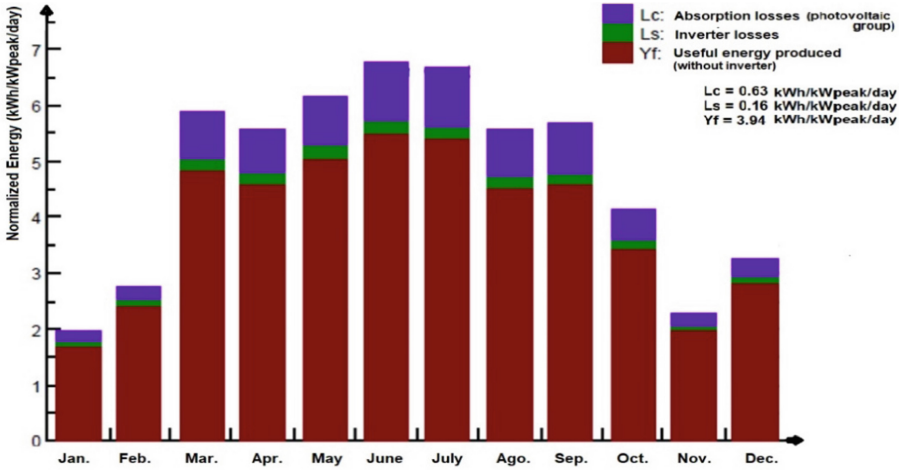


Fig. 8. Useful energy produced by the system in a self-consumption scenario.

4 Conclusion and Future Perspectives

It should be noted that practically all the equipment is in continuous operation in the greenhouse and in the scenario of energy production by self-consumption the investment is less than 8.000€ and it is possible to reduce the electric energy bill and sell the excess energy produced to the electricity grid, in accordance with the legislation. The scenario in an isolated network presents high costs and applied to this case study did not show great benefits.

The possibility for the greenhouse manager to have functionalities on his/her mobile phone to access data on key physical variables, allowing a real-time evaluation of the activity status is a guarantee of better efficiency and sustainability. The chosen equipment has good characteristics of useful life, reliability of operation, being the prototype installed in a professional level.

In the future, the air-cooling system should be improved, as well as the automation of opening/closing windows, and this process should be controlled and monitored according to the environmental conditions under study.

Also, as a future development, continuous and remote monitoring of energy consumption should be carried out and complementary sensors could be installed to increase the parameters collection. The prototype herein developed could be tested in greenhouses with other types of production technologies, to assess the performance under different conditions regarding its optimization and eventually large scale production.

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References

1. Accelerating SDG 7 Achievement Policy Briefs in Support of the First SDG 7 Review at the High-Level, Political, Forum 2018, United Nations. <https://sustainabledevelopment.un.org/content/documents/17483PB9.pdf>. Accessed 30 Dec 2020
2. Pires, T.C.S.P., et al.: Edible flowers as sources of phenolic compounds with bioactive potential. *Food Res. Int.* **105**, 580–588 (2018)
3. Ezzaeri, K., et al.: The effect of photovoltaic panels on the microclimate and on the tomato production under photovoltaic canarian greenhouses. *Sol. Energy* **173**, 1126–1134 (2018)
4. Galvão, J., Nabais, A., Correia, H., Amaro, P., Negrão, A., Ribeiro, V.: Intensive agriculture production in low consumption energy environment. *Renew. Energy Power Qual. J.* **17**, 354–359 (2019). ISSN 2172-038X. <https://doi.org/10.24084/repqj17.310>
5. Galvão, J., Correia, H., Amaro, P., Nabais, A., Galvão, M., Ribeiro, V.: The contribution of biomass for energy efficiency in greenhouses. In: 3rd Bioenergy International Conference, Portalegre, Portugal, Proceedings Conference eBook ISBN 978-84-17934-31-6,= (2019)
6. Maucieri, C., Nicoletto, C., Junge, R., Schmautz, Z., Sambo, P.: Hydroponic systems and water management in aquaponics. *Italian J. Agron.* **13**(1) (2018)
7. Taha, F., Osman, A., Awdalkareem, S., Omen, M., Saadaldeen, R., A Design of a Remote Greenhouse Monitoring and Controlling System Based on Internet of things. In: em International Conference on Computer, Control, Electrical and Electronics Engineering (2018)
8. Shamshiri, R., et al.: Advances in greenhouse automation and controlled environment agriculture: a transition to plant factories and urban agriculture. *Int. J. Agric. Biol. Eng.* **11**(1) (2018)
9. Galvão, J., Ascenso, R., Pereira, S., Moreira, L., Neves, F.: Smart energy in sustainable services building. In: da Costa Sanches Galvão, J.R., et al. (eds.) ICoWEFS 2021, pp. 421–430. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-75315-3_47
10. Pinto, P.: pplware (2019). <https://pplware.sapo.pt/tutoriais/networking/mqtt-protocolo-de-comunicacao/>. Accessed 12 Dec 2020
11. Random NERD Tutorials. <https://randomnerdtutorials.com/esp32-mqtt-publish-dht11-dht22-arduino/>. Accessed 21 March 2021
12. O’Leary, N.: Conway-Jones e Dave, “Node-RED. IBM Emerging Technology (2013). <https://nodered.org/>. Accessed 12 March 2021
13. Baiborodin e Pavel: Blynk, <https://blynk.io/>. Accessed 21 March 2021
14. Widenius e Michael: MariaDB (2009). <https://mariadb.org/>. Accessed 28 March 2021
15. Arduino (2005). <https://www.arduino.cc/en/software>. Accessed 10 Oct 2020



Energy Certification of Existing Residential Buildings: Adaptations to the Energy Transition

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Abstract. In Portugal, the energy certification of existing buildings is mandatory since 2009 in the sales or lease contract. This obligation, imposed by the first legislation of the SCE (Energy Certification System) was based on the Energy Performance of Buildings Directive from 2002. Since then, the SCE legislation has been undergoing constant changes. The last change concerns Decree-Law No. 101-D / 2020, with practical application from July 1, 2021.

More than a decade later and considering that the validity period of the energy certificate for residential buildings is ten years, the objective of this work is to present a reflection on the evolution of concepts and methodologies for calculating energy performance. The procedures for issuing the energy certificate, the content, and the graphic image, will also be analyzed. For this purpose, a single-family building, built in the 1990s and certified in November 2010, is used as an example.

Keywords: Energy certification · Residential · Existing buildings · Portugal

1 Energy Certification of Existing Buildings

1.1 Evolution of National Legislation on Energy Certification of Buildings

In Portugal, the first regulation on energy performance of buildings appeared in 1990 (RCCTE, Decree-Law n° 40/90). Although undemanding, it introduced the frequent practice and the growing interest in introducing thermal insulation in buildings [1].

To address the problems associated with the excessive consumption of fossil energy in buildings, the European Commission approved the directive on the energy performance of buildings, Directive 2002/91/EC (EPBD-2002). With it, came the following novelties: -Minimum requirements for the energy performance of major renovations; -Review of legislation at least every five years; -Recourse to renewable energy; - Adequate qualification of technicians for certification and installation of systems; - Energy Certification of Buildings [2]. Its transposition into national law was carried out by: - Decree-Law n° 78/2006, SCE (National System for Energy Certification and Indoor Air Quality in Buildings); -Decree-Law n° 79/2006, RSECE (Regulation of Energy Systems for Air Conditioning in Buildings); - and Decree-Law n° 80/2006, RCCTE (Regulation

of the Thermal Behavior Characteristics of Buildings), which revoked the Decree-Law n° 40/90 [3–5].

In 2010, EPBD-2002 was revoked by Directive 2010/31/EC (EPBD recast-2010). This new version included a set of new challenges, such as buildings with almost zero energy consumption from 2020 onwards [6]. Its transposition into national law took place through Decree-Law n° 118/2013, revoking the aforementioned legislative instruments [7]. This diploma brought together in a single document the Energy Certification System for Buildings (SCE), the Energy Performance Regulation for Residential Buildings (REH), and the Energy Performance Regulation for Commercial and Service Buildings (RECS). In 2016 there was a relevant change regarding the values of the thermal behaviour and efficiency requirements of technical systems. This change considered the cost-optimal studies carried out in Portugal, in accordance with the directive's recommendations.

Intending to further reduce greenhouse gas emissions, and with an even greater focus on rehabilitation and the use of renewable energies, the European Union approved directive 2018/844, of 30 May 2018, which amends the EPBD recast- 2010. This directive was transposed into Decree-Law no.101-D/2020 [8, 9].

Figure 1 summarizes the evolution of legislation referred above.

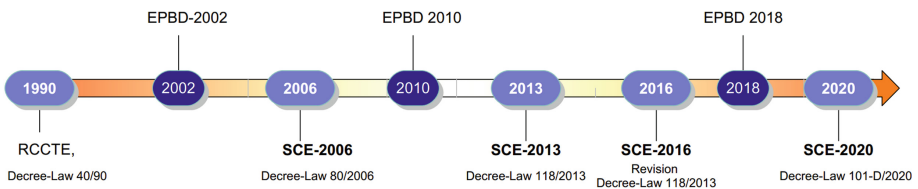


Fig. 1. Evolution of national legislation on Energy Certification of Buildings

1.2 The Energy Certification of Existing Buildings

The Energy Certificate (CE) allows future building users to obtain information on energy consumption and improvement measures. The CE classifies a residential building based on its integrated performance, which includes heating, cooling, and preparation of domestic hot water (DHW). The energy rating scale of buildings until 2013 was composed by 9 classes, A+, A, B, B–, C, D, E, F and G (class A+ corresponding to the best performance and G to the worst). After 2013 the G class disappeared.

The national energy certification of buildings took place in stages. First (in 2006) it became mandatory for new buildings, and in January 2009, it was extended to existing buildings [10]. As opposed to a new building, an existing building is understood to mean any building whose application date for construction license prior to the entry into force of the SCE legislation. In these cases, the building owner must be responsible for obtaining the CE to hand it over to the future owner or tenant, in the act of sale or lease. He will have to contract a Qualified Expert (PQ) to carry out the CE and providing him the necessary documentation for a good characterization of constructive and technical solutions of the building. In addition, the PQ must make a visit to the building.

Logically, there are no minimum requirements regarding the envelope, technical systems, and energy needs for existing buildings, as the assessment is made considering the characteristics of the building at the time of certification, assuming any of the classes mentioned above. The energy performance assessment of this type of building can be done using a simplified calculation method since it is not possible to determine all the solutions accurately [11–13]. However, the PQ should only use the simplification rules that it deems strictly necessary. These simplifications are related to the following items: -Dimensions; - Thermal bridges; - Loss reduction coefficient of non-useful spaces; - Mechanical ventilation; - Solar factor of the glazed span; - Thermal transmission coefficient; - Inertia class; - Solar energy; - Efficiency of systems; - Shading factors.

PQs must study the opportunities for improving the energy performance of building and registering them in the CE. These improving measures are very important, as they aim to guide owners to intervening in the building to increase thermal comfort and energy savings.

In the last years, Energy Certification was an important issue treated by several international studies [14–19]. Some of them, demonstrate flaws, such as the superficiality with which some subjects are treated, like the indoor air quality and health [17], and the comparison with the real energy consumption [18]. Also, the constant changes in legislation cause different values of energy needs calculation, which causes inconsistencies in the changes and discredits the system [19]. In any case, relative to EU countries, the implementation of the Energy Certification System was similar, although the need to adapt the methodologies to the climate zone.

As already mentioned, in Portugal, since 2009 certification of existing buildings has been mandatory, but only when selling or renting. As legislation has been continuously amended, there are similar buildings on the market built in the same year but certified in different years, subject to different calculation methodologies. Furthermore, the validity of CE Residential Buildings is ten years. Many buildings needs or will soon needs a new certificate for sale, lease or interventions included in financing programs. Previous and current CEs will be compared. It is important to take stock of the situation and reflect on the main changes.

2 Methodology

This study aims to analyze and reflect on the evolution of national legislation on the energy certification system applied to existing residential buildings. To this end, a case study of a typical single-family house certified by the SCE-2006 Methodology is used.

Then Certification is simulated using SCE-2013, SCE-2016 and SCE-2020 Methodologies. As it is an existing building, some simplifications allowed by legislation were used. In the end, calculation methodologies and results are compared.

3 Case Study

3.1 Description of Climate Data and Building Solutions

General Description. This case study is based on an existing single-family house built in 1990. It consists of a ground floor, comprising two living rooms, one kitchen, one toilet,

one pantry, one hallway and one stair, which communicates with the 1st floor comprising four bedrooms, one toilet and one corridor (all conditioned spaces). The ground floor is in contact with the land, and the 1st-floor ceiling is with an unconditioned attic. Laterally, the walls are in contact with another building. The main facade is oriented to the East. Most significant shading is caused by neighbouring buildings (Fig. 2).



Fig. 2. Location and facade of the building.

Climatic data and Location. The building is in Bragança city, in an urban area, at an altitude of 699 m, inserted in the Climatic Zone I3-V2.

Climate data have been updated over the years. Table 1 shows the main climatic data referring to the different methodologies.

Table 1. Climatic parameters.

<u>Climate Data, Bragança, 699 m</u>	SCE-2006	SCE-2013/2016/2020
Climate Zone (I, Winter e V, Summer)	I3-V2	I3-V2
Degree-days, GD (°C.dias)	2850	2042
Heating season duration (months)	8	7,3
Cooling season duration (months)	4	4
Average summer outdoor temperature (°C)	19	21,4
GSul (kWh/m2. Month) - Average solar energy incident on a south-facing vertical surface	90	125

Table 2 shows the average solar energy incident on a surface accumulated during the cooling season (June to September).

Table 2. Intensity of solar radiation for the cooling season.

	Solar Radiation Intensity for the Cooling Season, kWh/m2								
	N	NE	E	SE	S	SW	W	NW	Horizontal
SCE-2006	200	320	450	470	420	470	450	320	790
SCE-2013/2016/2020	220	345	480	485	425	485	480	345	790

Dimensional and Thermal Characterization. The exact dimensional survey of the building was conducted, which allowed the following information: Useful area (m2) = 148 m2; Average right foot = 2.6 m; Exterior walls = 108 m2; Interior walls = 66 m2; Glazed spans = 17 m2 (Fig. 3).

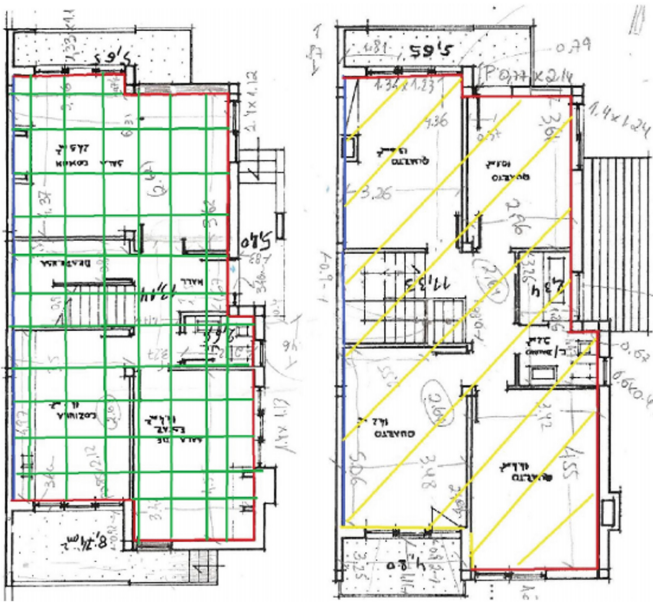


Fig. 3. Building plans.

The unconditioned spaces identified were: - Buffer zone; - Coverage attic; - Adjacent building. The methodology for determining the loss reduction coefficient for unconditioned spaces has been changed since SCE-2006.

For being a building built in 1990 (before the first thermal regulation), the absence of any thermal insulation in walls and floors was considered. The values of thermal transmission coefficient considered for the building envelope were: - Exterior walls, 34 cm, $U = 0.99$ (W/m2.°C); - Internal walls, 34 cm, $U = 0.91$ (W/m2.°C) and: - Interior roof, 20cm $U = 2.25$ (W/m2.°C).

It was impossible to identify if pillars and beams were isolated, so they were increased by 35% of the losses associated with the current envelope.

All situations of linear thermal bridges were identified and measured, and the simplifications provided for in the legislation were adopted. The methodology for this type of loss has changed from SCE-2006 to SCE-2013, with the latter increasing losses through these elements.

The material of windows/openings frames are in aluminium, without thermal break, 4mm single colourless glass, with the following values of thermal transmission coefficient: - $U = 3.9 \text{ W/m}^2\cdot\text{°C}$, for windows with rotating system and external blinds; - $U = 4.1 \text{ W/m}^2\cdot\text{°C}$, for windows with sliding system and external blinds; - $U = 6 \text{ W/m}^2\cdot\text{°C}$, for windows with a fixed system, without blinds, and - $U = 6.2 \text{ W/m}^2\cdot\text{°C}$, for windows with swivel system, without blinds.

The ventilation was natural without any systems. The methodology for calculating ventilation significantly changed with SCE – 2013/2016/2020 (air changes per hour, RPH = 0.99 h^{-1}) compared with the SCE-2006 Methodology (RPH: 0.73 h^{-1}). A spreadsheet developed by LNEC (National Civil Engineering Laboratory) was used.

Since it was impossible to know all the construction solutions, the average thermal inertia was considered using simplifications.

Energy Systems. As there weren't heating and cooling systems, default systems and efficiencies were considered (electrical resistance for heating and air conditioning for cooling). The existing system in the house for DHW was a natural gas boiler with natural ventilation and power of 17.4KW. The water pipeline was considered without isolation. Solar collectors or other renewable energy systems were not considered.

3.2 Analysis and Comparison of Energy Performance Results and Energy Certificate

The most relevant comparisons between the different methodologies are presented in this chapter. It should be noted that the SCE-2013 Methodology has changed significantly compared to the SCE-2006 Methodology. After that, the SCE-2016 and SCE-2020 Methodologies almost didn't change.

In winter (Heating Station), according to Fig. 4, Total Energy Losses was reduced after the SCE-2013 Methodology. That is because the number of GD (Degree-days)

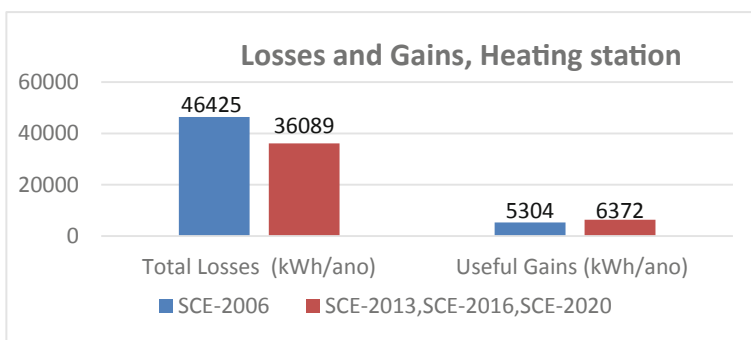


Fig. 4. Losses and gains, heating station.

(which reduced the losses by transmission and ventilation) and the air changes per hour, Rph parameter, (which reduced the losses by ventilation) were changed. Regarding Useful Heat Gains value, from the SCE-2013 onwards, there has been increasing. Internal Heat Gains decreased as the season months went from 8 to 7.3. But, although this value has decreased, the Solar Gains significantly increased because the radiation incident on glazing to the south (G_{sol}) went from 90 kWh/m².month to 125 kWh/m².month.

Regarding the summer (Cooling Station), analyzing Fig. 5, the Total Heat Losses are more significant from the SCE-2013 onwards. Although the Rph parameter has decreased and the average outdoor summer temperature has gone from 19°C to 21.4°C, the losses caused by the elements in contact with the ground and by the interior envelope are accounted for are relevant in this example. The Solar Gains by the opaque envelope also increased significantly due not only to the increase in the values of the Intensity of solar radiation but essentially due to the accounting of the interior coverage.

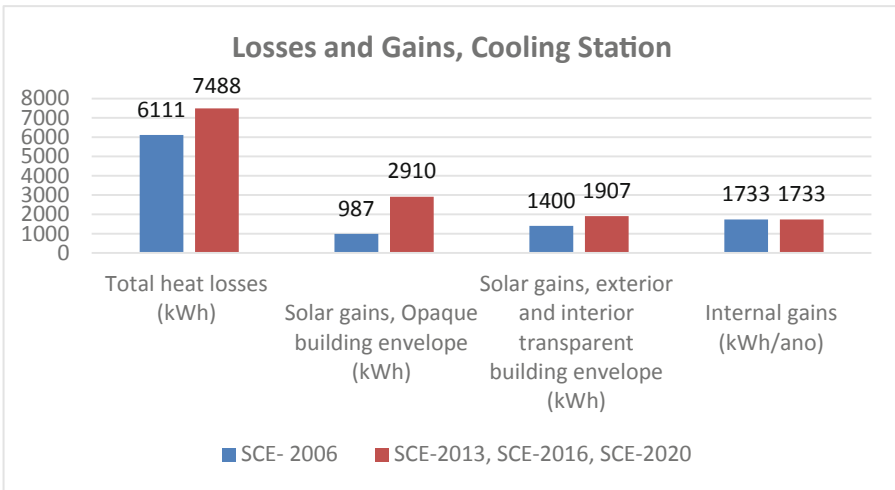


Fig. 5. Losses and gains, cooling station.

In summary, Table 3 shows the values of: - Nominal Useful Energy required for Heating (N_{ic}) and Nominal Useful Energy required for Heating of Reference (N_i); - Nominal Useful Energy required for Cooling (N_{vc}) and Nominal Useful Energy required for Cooling of Reference (N_v).

From the SCE-2013 onwards, a decrease in the value of N_{ic} has been observed. This is because the solar gains of the Building are much higher than the Reference Building. The ratio between N_{vc} and N_v is close to unity from the SCE-2013 onwards.

Concerning the Nominal Useful Energy required for Heating Domestic Hot Water (Q_a/A_p), as we can see in Table 4, since SCE-2013, there has been a decrease in its value because the required temperature has gone from 60°C to 50°C.

Table 5 presents the energy classes referring to the different methodologies. The energy class is obtained from the ratio between Nominal Primary Energy Needs and its Reference value (N_{tc}/N_t). Although the SCE-2013, 2016 and 2020 methodologies are

Table 3. Energy needs for heating and cooling.

	SCE- 2006	SCE-2013	SCE-2016	SCE-2020
Nic (kWh/m2.year)	277,85	200,74	200,74	200,74
Ni (kWh/m2.year)	125,60	101,98	82,12	90,06
Nic/Ni	2,21	1,97	2,44	2,23
Nvc (kWh/m2.year)	4,29	10,24	10,24	10,24
Nc (kWh/m2.year)	18	10,6	10,6	10,6
Nvc/Nv	0,24	0,97	0,97	0,97

Table 4. Energy Need for Heating Domestic Hot Water.

	SCE- 2006	SCE-2013	SCE-2016	SCE-2020
Qa/Ap (kWh/m2.ano)	30,98	24,09	24,09	24,09

similar, there are differences in values and reference formulas adjusted over the years and which cause different energy classes. The difference between the SCE-2006 and SCE-2013 methodologies is not reflected in the Energy Class. Despite the differences in various parameters and calculation indices, as detailed above, the overall balance between thermal losses and gains is reflected in the same class, in this specific building.

The table also shows the value of CO₂ emissions. We can observe an increase in its value from the SCE-2013 onwards, due to the different calculation methodologies of this parameter.

Table 5. Classes and CO₂ emissions.

	SCE- 2006	SCE-2013	SCE-2016	SCE-2020
Ntc/Nt	1,9	2,0	2,4	2,2
ENERGY CLASS	D	D	E	E
CO ₂ (t/year)	2,6	12,5	12,5	12,5

Regarding the CE, the SCE-2013 brought some changes in terms of its structure and information, with the objective of facilitating its interpretation, which resulted in a clear separation of information intended for the consumer and the professional. For the consumer, the changes are essentially related to the simplification of information and the incorporation of performance benchmarks, with a more appealing layout.

4 Conclusion

The SCE-2006 Methodology has undergone substantial changes compared to the SCE-2013/2016/2020 Methodologies. In addition to the methodological aspects, there are relevant differences regarding climate data, demonstrating an increase in temperatures tabulated from SCE-2013 onwards.

For the climate zone in question (I3-V2), to which Bragança belongs, these differences have an impact mainly on the level of heating energy needs (N_{ic}), with the SCE-2013 obtaining a much lower value. However, this is not the reason why this station is no longer a concern in terms of verifying energy requirements, as the reference value (N_i) also has lower values.

About summer station, from SCE-2013 onwards, significantly higher values of useful energy requirements for cooling are recorded. The N_{vc}/N_v ratio tends to approach unity.

Relating to DHW, the required temperature has gone from 60°C (SCE-2006) to 50°C (from SCE-2013), which makes the energy requirements have lower values after SCE-2013.

The comparison with the reference building (which only came into existence after the 2013-SCE) is advantageous, as it allows for a better focus on opportunities for improving the real building. The introduction of reference values in the CE information is also practical to compare with the values of the real building.

In summary, as of SCE-2013, in total primary energy, the weight of energy needs for heating and cooling has increased, and the weight of energy for hot water production has decreased. This change is positive and more adapted to the natural energy consumption of buildings in the climatic zone analyzed in this study. Furthermore, the fact that the winter comfort temperature has been reduced from 20°C to 18°C (changing GD value) allows a better comparison with reality use and a better understanding about the improvement measures constant in the CEs.

Improvement measures play an essential role to guide owners in interventions. CEs are important information vehicles for these interventions. In addition, the information contained in the CE is used so that buyers or tenants can compare homes. Over the last ten years of mandatory certification of existing buildings, there have been constant changes in the methodologies applied, which have resulted in different values of energy indices, including different energy classes, which makes it difficult for owners to perceive the different certificates and their comparison for buying or renting a house. Although the CEs contain information regarding the applied methodologies, it is essential to clarify the owners and users about these differences. In addition, the constant changes in legislation do the work of those involved, especially the PQs, more time consuming due to the constant need for updating.

References

1. Decreto-Lei n.º 40/90 de 6 de fevereiro, Regulamento das Características de Comportamento Térmico dos Edifícios (1990)
2. European Parliament and of the Council, Directive 2002/91/EC - Energy performance of buildings. Brussels (2002)

3. Decreto-Lei n.º 78/2006, de 4 de abril, Sistema Nacional de Certificação Energética e da Qualidade do Ar Interior nos Edifícios (2006)
4. Decreto-Lei n.º 79/2006 de 4 de abril, Regulamento dos Sistemas Energéticos de Climatização em Edifícios (2006)
5. Decreto-Lei n.º 80/2006 de 04 de abril, Regulamento das Características de Comportamento Térmico dos Edifícios (2006)
6. European Parliament and of the Council, Directive 2010/31/EU - Energy performance of buildings. Brussels (2010)
7. Decreto-Lei n.º 118/2013 de 20 de agosto, Sistema de Certificação Energética dos Edifícios, Regulamento de Desempenho Energético dos Edifícios de Habitação e Regulamento de Desempenho Energético dos Edifícios de Comércio e Serviços (2013)
8. European Parliament and the Council, Directive (EU) 2018/844, amending Directive 2010/31/EU regarding the energy performance of buildings. Brussels (2018)
9. Decreto-Lei n.º 101-D/2020, de 7 de dezembro, Requisitos aplicáveis a edifícios para a melhoria do seu desempenho energético e regula o Sistema de Certificação Energética de Edifícios (2020)
10. Portaria n.º 461/2007 de 05 de junho, Calendarização da Aplicação do Sistema de Certificação Energética e da Qualidade do Ar Interior dos Edifícios (2007)
11. Despacho n.º 11020/2009 de 30 de abril, Método de Cálculo Simplificado para a Certificação Energética de Edifícios Existentes no âmbito do RCCTE (2009)
12. Despacho (extrato) n.º 15793-E/2013, Regras de simplificação a utilizar nos edifícios sujeitos a grandes intervenções, bem como existentes (2013)
13. Despacho n.º 6476-H/2021, de 1 de julho, Manual SCE, Manual Técnico para a Avaliação do Desempenho Energético dos Edifícios (2021)
14. De Lieto, R., Vollaro, C.G., Evangelisti, L., Battista, G., Carnielo, E., Gori, P.: Building energy performance analysis: a case study. *Energy and Buildings* **87**, 87–94 (2015)
15. Casals, X.G.: Analysis of building energy regulation and certification in Europe: their role, limitations and differences. In: *Energy Build.* **38**, pp. 381–392 (2006)
16. Perez-Lombard, L., Ortiz, J., Gonzalez, R., Maestre, I.R.: A review of benchmarking, rating and labelling concepts within the framework of building energy certification schemes. In: *Energy Build* **41**, pp. 272–278 (2009)
17. Alabid, J., Bennadji, A., Seddiki, M.: A review on the energy retrofit policies and improvements of the UK existing buildings, challenges and benefits. In: *Renewable and Sustainable Energy Reviews* **159**, 112161 (2022)
18. Zuhair, S., et al.: Next-generation energy performance certificates: end-user needs and expectations. *Energy Policy* **161**, 112723 (2022)
19. Vaquero, P.: Buildings energy certification system in Portugal: ten years later. In: *Energy Reports* **6**(1), 541–547 (2020)



Energy Rehabilitation of Residential Buildings: Proposed Solutions for Bragança City

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Abstract. Portugal is committed to achieving carbon neutrality by 2050, intending to comply with the Paris Agreement on climate change and global warming. Renovating existing buildings is particularly relevant for decarbonization, and the long-term renovation strategy (LTRS) defines how to achieve this goal.

In Bragança city, more than 50% of the existing buildings are recent, built after 1981, and only 6% of them consider the first regulation based on the Energy Performance of Buildings Directive. It can be concluded that there is a considerable number of buildings, built without any legislation or based on poor thermal legislation, which requires adaptations to the new requirements of thermal comfort and energy performance in the coming years.

Based on a study of the residential energy buildings characterization in the city of Bragança, this work intends to present a set of intervention proposals to improve their energy efficiency, meeting the requirements of recent national legislation on the energy performance of buildings following the LTRS Principles.

Keywords: Energy rehabilitation · Residential buildings · Portugal · Bragança

1 Introduction

Nowadays, there is a consensus in the scientific community that the progressive increase in greenhouse gas (GHG) emissions over the last 100 years has increased the planet's temperature, causing undesirable climate changes. The latest report by the Intergovernmental Panel on Climate Change predicts a global temperature rise of 2.7 degrees by 2100 if the current pace of GHG emissions is kept [1]. The Paris Agreement, adopted in 2015, set the aim of continuing efforts to limit the average increase in global temperature to 1.5 °C, recognizing that this would significantly reduce the risks and impacts of climate change [2]. For that, it will be necessary to achieve carbon neutrality in the second half of this century. In line with this, the European Commission (EC) presented, in November 2016, the Clean Energy Package to promote the energy transition in the coming decades, and Portugal, as an EC member, assumed the commitment to achieve carbon neutrality by 2050 through the approval of the Roadmap for Carbon Neutrality 2050. To precisely fulfil the objectives of decarbonization and the energy transition, the

National Energy Climate Plan was approved (PNEC 2030), with measures for the 2030 horizon [3, 4].

Relative to buildings, PNEC 2030 sets out specific lines of action, including promoting energy renovation in the building stock. Research of EU residential building stock [5] shows that environmental impact from new buildings is negligible compared to the impact from existing buildings. The European Ecological Pact also drives renovation of buildings, with a new strategy called “A Renovation Wave for Europe - greening our buildings, creating jobs, improving lives” [6]. These lines of action aimed at the construction sector, namely existing buildings, are essential. In Portugal, as in other countries of the European Union, buildings are responsible for about 30% of final energy consumption and 5% of GHG emissions [3]. In this sense, the Energy performance of buildings directive determines the obligation of each Member State to establish a long-term strategy to support the renovation of buildings until 2050 (LTRS) [7]. The objective will be to convert the existing building stock into decarbonized and highly energy-efficient, transforming existing buildings into Nearly Zero Energy Buildings (NZEB) [7, 8]. Financing programs and incentive policies are necessary [9] and planned to encourage this energy transformation, so dynamism is expected in the coming decades. Specifically, the measures to be taken in existing buildings included in the LTRS are: - intervention in the building envelope; - replacement existing systems; - and promotion energy from renewable sources. It should be noted that priority should be given to the building envelope [10], with a significant environmental improvement potential, which, for a majority of buildings, represents at least 20% compared to the base case [5, 11]. The variation in the thermal insulation thickness implies a great variation in the total primary energy consumption and better cost-efficient results is obtained from insulating Roofs [12]. In Portugal, most interventions in this field, as they are isolated acts, do not need a project. In this way, decisions pass to the owners and builders, with little training in the area, missing unique opportunities to improve the building stock’s energy efficiency effectively.

In this sense, this study aims to present proposals for energy rehabilitation in the building envelope, meeting the identified needs. It is focused on residential buildings of Bragança city. Bragança serves as an excellent example because more than 50% of the existing buildings are recent, built after 1981. Only 6% of them consider the first regulation based on the Energy Performance of Buildings Directive [13]. It can be concluded, like in other European countries [14], that there is a considerable number of buildings, built without any legislation or based on poor thermal legislation, which requires adaptations to the new thermal comfort and energy performance requirements in the coming years.

2 Methodology

The intervention proposals presented in this study intend to follow up another study with contributions to the energy characterization of residential buildings in Bragança [13]. This characterization was based on statistical data analysis, expert interviews, and the study of 250 residential buildings, energy certified, belonging to the 1980s, 1990s and 2000s.

The intervention proposals are accompanied by tables, which summarize the characteristic solutions of the opaque building envelope (walls, floors and roofs) and windows, with the thickness of elements presented in cm. It was intended to fit the requirements of the existing buildings to current requirements. The necessary thermal insulation thickness was calculated using average market values (thermal conductivity coefficient: 0.0300.04 W/mK) to verify the maximum ($U_{Max.}$) and reference ($U_{Ref.}$) thermal transmission coefficients required by the current legislation, the Decree-Law 101-D/2020 [15].

The buildings are separated by different construction periods according to the evolution of the thermal legislation:

- Years of Construction: 1980–1992, buildings built without any thermal legislation (Before RCCTE).
- Years of Construction: 1993–2008, buildings built by Decree-Law n° 40/90 (RCCTE-1990) [16]. This regulation is responsible for the beginning of placing thermal insulation in the building envelope, especially in walls.
- Years of Construction: after 2008, buildings built by Decree-Law n° 80/2006, with stricter thermal requirements than RCCTE-1990 (RCCTE-2006) [17].

It is important to note that the thermal legislation was reflected in the construction approximately two years later. Beyond the evolution of legislation, the evolution of market construction was also considered. For example, only from the 2000s onwards, a better aluminium frame, with thermal break, characterizes the windows. At the beginning of this decade, PVC (polyvinyl Chloride) frame also emerged as a recurring option. The separation in two types of building – multi-family and single-family – was only made for the construction period “RCCTE-2006, after 2008” because only in this period the divergence between the two began to have an impact.

The intervention proposals presented in this study are based on the suggested improvements of energy certificates and the solutions available on the market. In addition, technical, functional, and economic aspects were analyzed.

3 Intervention Proposals





3.1 External Walls

External walls before RCCTE-2006, especially from the 1980s have a huge potential for intervention through incorporating thermal insulation, as can be seen in Table 1.

Insulation can be applied outside, inside, or into the air space. In rehabilitation, the ETICS system (External Thermal Insulation Composite Systems) is the most used system from the outside, having a lower cost than most external systems, is easier to apply, and has less impact at an aesthetic level. Despite being a solution with a higher cost, Ventilated Facades can have advantages in adding aesthetic value and not interfering with the existing coating.

Exterior insulation systems have the advantage of maintaining the building’s thermal inertia and treating sensitive areas, such as pillars and beams, and linear thermal bridges

Table 1. External wall solutions

Construction age	Before RCCTE	RCCTE- 1990	RCCTE- 2006	
	1980-1992	1993-2008	After 2008	
External walls, solutions for construction periods				
Characteristic solution U [W/m ² .° C]	Brick15+ Air space + Brick11 U=1	Brick15+ Air space+ XPS3+ Brick11 U=0,57	multi-family building	single-family building
			Brick15+ Air space + XPS4+ Brick11 U=0,5	Brick15+ Air space + XPS6+ Brick11 U=0,4
U Max. = U Ref.	U=0,35			
Thermal bridges, pillars,...isolated?	No	No	Yes	Yes
Isolation to achieve U Máx/Ref	6cm - 8cm	3cm - 5cm	2cm - 4cm	2cm

through the continuity of the insulation. However, an agreement condominium is necessary in multi-family buildings. When this does not happen, when it is impossible to change the aesthetics of the building, or when it is technically challenging to carry out the work, insulation from the inside (placed directly on the wall or forming a structure with an air gap) is an option. The most common thermal insulations are expanded polystyrene (EPS), extruded (XPS), cork, glass wool or rock wool. One must be selective in choosing these materials, as some incentive programs for renovating buildings are committed to environmental sustainability. It will be guaranteed through the choice of eco-materials or recycled materials.




In double walls without thermal insulation, incorporating loose insulating materials or injecting insulation foam in the air space can be presented as a solution. However, although it is an easy and economical solution, it offers fewer guarantees of insulation continuity (due to the possible existence of reduced air thickness of the debris). Single constructive elements, such as pillars and beams, are not isolated. In addition, it is a wrong solution in terms of linear losses and also poses difficulties in terms of quality control of the work.

3.2 Internal Walls

Internal wall solutions (which separate conditioned spaces from unconditioned spaces) from the 1980s and, in general, interior wall solutions in contact with garages, laundry rooms, buffer zones and attics are the ones with the greatest potential for intervention through the incorporation of thermal insulation.

Table 2 demonstrates the Internal wall solutions by the different construction periods.

Table 2. Internal wall solutions





Construction age	Before RCCTE	RCCTE- 1990	RCCTE- 2006
	1980-1992	1993-2008	After 2008
Internal wall solutions			
Characteristic solution U [W/m ² .° C]	<p>Adjacent buildings Brick 11/15+ air space+Brick11 U=0,88</p> <p>Common zones Brick 15 U=1,5</p> <p>Laundry/Storage/Buffer zones/Attics Brick 11 U=1,9</p>	<p>Adjacent buildings Brick 11/15+ air space+XPS3+ Brick11 U=0,55</p> <p>Common zones Brick 11+XPS3+ Brick11 U=0,65</p> <p>Laundry/Storage/Buffer zones/Attics Brick 11 U=1,9</p>	<p>Adjacent buildings Brick 11/15+ air space+XPS4+ Brick11 U=0,48</p> <p>Common zones Brick 11+XPS3+ Brick11 U=0,65</p> <p>Laundry/Storage/Buffer zones/Attics a) Brick 15 U=1,5 (bztu ≤ 0,7) b) Brick 7+XPS4+ Brick7 U=0,58 (bztu > 0,7)</p>
U Max. [W/m ² .° C]		U=1,9 (bztu ≤ 0,7) U=0,35 (bztu > 0,7)	
U Ref. [W/m ² .° C]		U= 0,6 (bztu ≤ 0,7) U= 0,35 (bztu > 0,7)	
Thermal bridges, pillars,...,isolated?	No	No	Yes
Isolation to achieve U Máx.	<p>Adjacent buildings -</p> <p>Common zones 8cm-10cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics 8cm-10cm (bztu > 0,7)</p>	<p>Adjacent buildings -</p> <p>Common zones 4cm-6cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics 8cm-10cm (bztu > 0,7)</p>	<p>Adjacent buildings -</p> <p>Common zones 4cm-6cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics a) - b) 3cm-5cm (bztu > 0,7)</p>
Isolation to achieve U Ref. <i>XPS/EPS/Mineral wool/cork (...)</i>	<p>Adjacent buildings 2cm-3cm</p> <p>Common zones 3cm-4cm (bztu ≤ 0,7) 8cm-10cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics 4cm-5cm (bztu ≤ 0,7) 8cm-10cm (bztu > 0,7)</p>	<p>Adjacent buildings -</p> <p>Common zones 1cm (bztu ≤ 0,7) 4cm-6cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics 4cm-5cm (bztu ≤ 0,7) 8cm-10cm (bztu > 0,7)</p>	<p>Adjacent buildings -</p> <p>Common zones 1cm (bztu ≤ 0,7) 4cm-6cm (bztu > 0,7)</p> <p>Laundry/Storage/Buffer zones/Attics a) 3cm-4cm (bztu ≤ 0,7) b) 3cm-5cm (bztu > 0,7)</p>
<p><i>bztu > 0,7- spaces with temperatures close to the outside temperature: U_{máx} is de same as the external walls.</i></p> <p><i>Adjacent Builings: bztu = 0,6</i></p>			

In the case of internal walls, it is not necessary to consult the condominium in most cases. The profitability of incorporating insulation will generally be more significant in these cases: -in older buildings; -with lighter or damaged coatings; -when the insulation does not reduce the useful area; - and when the contact of the non-conditioned space (like a laundry or a storage) with the outside is significant. As a rule, energy performance is better if the insulation is applied to the outside of the wall. There are prefabricated insulated solutions that are an excellent solution for interior spaces.

3.3 Floors and Roofs

According to Table 3, there is a significant energy savings potential incorporating thermal insulation in the roofs and floors of buildings before the RCCTE-2006, especially in single-family buildings where the decision is made by the owner, without intervention

Table 3. Roof and floor solutions

Construc- tion age	Before RCCTE	RCCTE- 1990	RCCTE- 2006	
	1980-1992	1993-2008	After 2008	
Roofs and Floors, Solutions				
			multi-family building	single-family building
Character- istic solu- tion U [W/m ² .° C]	<u>Ceilings below attics</u> Lightened slab 20cm U=2,25	<u>Ceilings below attics</u> Lightened slab 30cm U=1,87	<u>Ceilings below attics</u> Lightened slab 30cm + XPS 6cm U=0,46	<u>Ceilings below attics</u> Lightened slab 30cm + XPS 8cm U=0,37
	<u>External Floors</u> Lightened slab 25cm U=2,0	<u>External Floors</u> Lightened slab 40cm U=1,4	<u>External Floors</u> Lightened slab 40cm+ XPS/Mineral wool 3cm U=0,68	<u>External Floors</u> Lightened slab 40cm+ XPS/Mineral wool 4cm U=0,58
	<u>Internal Floors</u> Lightened slab 25cm U=1,6	<u>Internal Floors</u> Lightened slab 40cm U=1,2	<u>Internal Floors</u> Lightened slab 40cm+ XPS/Mineral wool 3cm U=0,64	<u>Internal Floors</u> Lightened slab 40cm+ XPS/Mineral wool 4cm U=0,54
U Max. [W/m ² .° C]	U=1,2 (bztu ≤ 0,7) U= 0,3 (bztu > 0,7)			
U Ref. [W/m ² .° C]	U= 0,5 (bztu ≤ 0,7) U= 0,3 (bztu > 0,7)			

(continued)

Table 3. (continued)

Construction age	Before RCCTE	RCCTE-1990	RCCTE- 2006	
	1980-1992	1993-2008	After 2008	
			multi-family building	single-family building
Isolation to achieve U Máx. <i>XPS/EPS/Mineral wool/cork (...)</i>	<u>Ceilings below attics</u> 2cm (bztu \leq 0,7) 9cm-12cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 1cm (bztu \leq 0,7) 9cm-11cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 3cm-5cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 1cm-3cm (bztu $>$ 0,7)
	<u>External Floors</u> 9cm - 12cm	<u>External Floors</u> 8cm-11cm	<u>External Floors</u> 5cm-8cm	<u>External Floors</u> 4cm-7cm
	<u>Internal Floors</u> 1cm (bztu \leq 0,7) 8cm-11cm (bztu $>$ 0,7)	<u>Internal Floors</u> 8cm-10cm (bztu $>$ 0,7)	<u>Internal Floors</u> 5cm-7cm (bztu $>$ 0,7)	<u>Internal Floors</u> 4cm-6cm (bztu $>$ 0,7)
Isolation to achieve U Ref. <i>XPS/EPS/Mineral wool/cork (...)</i>	<u>Ceilings below attics</u> 5cm-7cm (bztu \leq 0,7) 9cm-12cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 5cm-6cm (bztu \leq 0,7) 9cm-11cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 3cm-5cm (bztu $>$ 0,7)	<u>Ceilings below attics</u> 1cm-3cm (bztu $>$ 0,7)
	<u>External Floors</u> 9cm-12cm	<u>External Floors</u> 8cm-11cm	<u>External Floors</u> 5cm-8cm	<u>External Floors</u> 4cm-7cm
	<u>Internal Floors</u> 5cm-6cm (bztu \leq 0,7) 8cm-11cm (bztu $>$ 0,7)	<u>Internal Floors</u> 4cm-6cm (bztu \leq 0,7) 8cm-10cm (bztu $>$ 0,7)	<u>Internal Floors</u> 1cm (bztu \leq 0,7) 5cm-7cm (bztu $>$ 0,7)	<u>Internal Floors</u> 4cm-6cm (bztu $>$ 0,7)
<i>bztu > 0,7- spaces with temperatures close to the outside temperature: Umáx is de same as the external walls</i>				





by the condominium. Furthermore, in the latter case, the intervention is more uncomplicated, and as the ceiling height is usually higher, it allows more flexibility with the thickness of the floors.

In most cases, it is by insulating the non-habitable attic from the roof (preferably placing the insulation on the slab) that more significant energy savings and shorter pay-back times are achieved, since: - attics have temperatures very close to the outside; - the area of intervention is important; -and the measure is economical (in most cases it is enough to place only the insulating, without functional and aesthetic interferences). In addition, it must be ensured that the roofs have ventilation openings, preferably controllable (to open in summer, prevent overheating and close in winter, reducing heat losses). Choosing light colours and low emissivity coatings help to reduce summer energy needs.

3.4 Windows

As can be seen from the Table 4, the most significant potential for windows/openings intervention is mainly found in buildings from the 1980s (before the RCCTE-1990).

Table 4. Window solutions

Construction age	Before RCCTE	RCCTE- 1990		RCCTE- 2006
	1980-1992	1993-2000	2000-2008	After 2008
Windows solutions for construction periods				
Characteristic solution U [W/m ² .° C]	Aluminum frame without thermal break, sliding, light color, single glazing 4mm Plastic exterior blinds U=4,1 (some windows without protections: U=6,5)	Aluminum frame without thermal break, sliding, light color, double glazing 5+8+4mm Plastic exterior blinds U=3,1 (some windows without protections: U=4,4)	Aluminum frame with thermal break, tilting window, light color, double glazing 5+12+4mm Plastic exterior blinds U=2,58 (some windows without protections: U=3,5)	PVC or Aluminum frame with thermal break, tilting window, light color, double glazing 6+16+5mm Plastic exterior blinds U=2,1/2,5 (some windows with internal protections: U=2,7/3,3)
U Max. = U Ref. [W/m ² .° C]	U=2,2			

The contribution of windows depends on the frame, glass, and shading devices. In winter, they can cause significant thermal losses, and in summer, they can be responsible for internal overheating problems. In extensive renovations, changes dimensions and location of windows should be studied. Preference should be given to south-facing windows, sizing the shading devices well. The north and west windows must be minimal. When the frame is still in a good state of repair and there is space for placing another frame, the double system will provide good reinforcement of the thermal resistance. However, it may reduce the light transmissivity, be unsightly, and in summer, it may contribute to overheating because of the air gap between the windows. If the frame is in poor condition, the best solution will be its replacement, adopting solutions with better thermal performance.

As for the opening system, tilt and turn systems, in addition to having lower air permeability, allow for more effective ventilation control. One of the most important aspects to consider is the solar factor regarding glass replacement. The current double glazing, with an air gap of about 16 mm, is in most cases a good solution due to

improved insulation and reduced risk of condensation. Although less economical, there are solutions with argon or low emissivity double glazing. In terms of solar protection systems, in addition to other functions (light control and privacy), they prevent spaces from overheating in summer and reinforce the window's thermal resistance. Preferably, they should be placed outside the window, with light colors as they reduce the incidence of solar radiation.

Blind boxes are sensitive to air infiltration and have a low thermal resistance. The incorporation of thermal insulation in buildings before the RCCTE-2006 provides improvements in terms of energy performance and thermal comfort. If there is space, insulation can be incorporated inside the box, resulting in a simple, quick, economic measure that does not interfere with the aesthetics of the adjacent areas.

3.5 General Considerations

Any intervention must be used to intervene and requalify thermally and energetically. Therefore, a prior technical-economic assessment of possible solutions is essential. Some of these are only viable when deep intervention is needed. It should be noted that other factors, such as thermal comfort or even the aesthetic aspect, must be considered.

Quality assurance in the application and installation of systems must be based on the proper qualification and responsibility of the installers. Likewise, certified materials guarantee the quality and durability of the systems.

Sometimes, the real solutions of the building envelope are not those considered in the energy certificate. Due to lack of information, solutions may have been considered by default, mainly in buildings corresponding to the period from 1992 to 2004. For a more specific characterization, non-destructive "in-situ" measurement tools with Thermographic Cameras and Heat Flow Sensors can be used.

4 Conclusions

The goals for the energy transition, together with the clear trend towards the rehabilitation of buildings, will undoubtedly be reflected in more demanding legislation and instruments to support energy efficiency, serving as levers to improve the energy performance of existing buildings.

In Bragança, many buildings were built without any legislation or based on a poor legislation, requiring interventions and adaptations to the new thermal and energy comfort requirements in the coming years. These buildings, before the RCCTE-2006, are essentially characterized by a reinforced concrete structure, double walls with low thermal insulation thicknesses in the air space and the absence of thermal insulation in most of the remaining constructive elements. In addition, the buildings before the RCCTE-1992 are characterized by sliding window frames systems and single glass. This type of construction provides sensitive and unique areas, causing discomfort and significant thermal losses. So, there is considerable potential for energy savings if the renovation of buildings is carried out efficiently. The reinforcement of the thermal resistance of the various constructive elements deserves special attention, namely on the roofs. It should

be noted that the building envelope and passive systems should assume more importance to the detriment of technical systems.





Interventions in existing buildings are often isolated measures without a thermal project and without prior control by city councils, technicians, and specialists. However, these interventions should allow existing buildings to become NZEB buildings in the future. It is essential to provide more information, especially for owners and builders, to adopt best practices and prevent these frequent interventions from being a waste of improvement opportunities in the coming years.

References

1. Intergovernmental panel of Climatic Change, IPCC, Climatic Change 2021 (2021)
2. United Nation, Paris Agreement 2015 (2015)
3. RNC 2050, Roadmap for carbon neutrality 2050, Long-term strategy for carbon neutrality of the Portuguese economy by 2050 (2019)
4. PNEC 2030, Plano Nacional de Energia e Clima, Resolução do Conselho de Ministros n.º 53/2020, 10 julho 2020 (2020)
5. Nemry, F., et al.: Options to reduce the environmental impacts of residential buildings. In: The European Union-Potential and Costs, Energy and Buildings **42**(7), 976–984 (2010)
6. <https://eur-lex.europa.eu>, COM(2020) 662, A Renovation Wave for Europe - greening our buildings, creating jobs, improving lives. Access 10 Mar 2022
7. European Parliament and the Council, Directive (EU) 2018/844, amending Directive 2010/31/EU regarding the energy performance of buildings and Directive (2018)
8. ELPRE, Estratégia de Longo Prazo para a Renovação dos Edifícios, 03 de fevereiro de 2021, Resolução do Conselho de Ministros n.º 8-A/2021 (2021)
9. Zhang, H., Hewage, K., Karunathilake, H., Feng, H., Sadiq, R.: Research on policy strategies for implementing energy retrofits in the residential buildings. In: Journal of Building Engineering **43** (2021)
10. Aelenei, L., et al.: Design issues for net zero-energy buildings. In: Open House International **38**(3), 7–14 (2013)
11. Sadineni, S.B., Madala, S., Boehm, R.F.: Passive building energy savings: a review of building envelope components. In: Renewable and Sustainable Energy Reviews **15** (2011)
12. de Vasconcelos, A.B., Pinheiro, D.M., Manso, A., Cabaço, A.: EPBD cost-optimal methodology: application to the thermal rehabilitation of the building envelope of a Portuguese residential reference building. In: Energy and Buildings **111**, 12–25 (2016)
13. Fernandes S.: Contributos para a caracterização energética de edifícios habitacionais do concelho de Bragança. In: CIEEMAT, III Congresso Ibero-Americano de Empreendedorismo, Energia, Ambiente e Tecnologia, Instituto Politécnico de Bragança (2017)
14. Iralde, N. S.I., Pascual, J., Salom, J.: Energy retrofit of residential building clusters. a literature review of crossover recommended measures, policies instruments and allocated funds in Spain, Energy and Buildings **252** (2021)
15. Decreto-Lei n.º 101-D/2020, de 7 de dezembro - Estabelece os requisitos aplicáveis a edifícios para a melhoria do seu desempenho energético e regula o Sistema de Certificação Energética (2020)
16. Decreto-Lei n.º 40/90 de 6 de fevereiro, Regulamento das Características de Comportamento Térmico dos Edifícios (1990)
17. Decreto-Lei n.º 80/2006 de 04 de abril, Regulamento das Características de Comportamento Térmico dos Edifícios (2006)



Using Machine Learning to Identify Solid Biofuels

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Abstract. To achieve the transition from a linear economy to a circular bioeconomy, a full implementation of the biorefinery concept is needed. The sustainability of biorefineries requires knowledge of the characteristics of sitespecific biomasses and residual biomasses. However, the complexity, variability and seasonality of biomasses pose huge challenges to the conception, assessment and management of biorefinery installations. In this context the classification of biomasses based on machine learning approaches and using proximate analysis data may be helpful in the decision-making process and management of biorefinery units. On the other hand, automatic identification of the sources of solid biofuel material might be advantageous in the context where the material has already been processed and must be used in energy generation or as raw materials of a biorefinery scheme, or when the elementary contents of the materials might not be existent or easily available. In this work, we use a public dataset to build classification models to predict the solid biofuel type from their fixed carbon, volatile matter, and ash contents. The dataset aggregates 585 examples of solid biofuels classified as one of four different types: coals, woods, agriculture residues, and manufactured biomass. Since the dataset presents a strong imbalance towards one of the classes, an algorithm to promote class balancing with synthetic oversampling is used. Then, six different models for biofuel classification are built, tested, and validated. The analysis of the relative contribution to each of the features for the final model is performed. The results show that it is possible to achieve an overall classification accuracy of 90%.

Keywords: Solid biofuels · Biorefinery · Machine learning · Multi-class classification · Random forest · Extreme gradient boosting

1 Introduction

To achieve the transition from a linear economy, based mainly on fossil resources, to a circular bioeconomy, based on renewable resources, a full implementation of the biorefinery concept is needed. Biorefinery is the sustainable integration of processes

to transform biomasses into a portfolio of biofuels, bioenergy, and bioproducts, while minimizing or zeroing residues generation [1]. But the ecological, economic, and technological sustainability of biorefineries will require the knowledge of the characteristics of site-specific biomasses and residual biomasses, since ideally generation of energy and production of goods should be decentralized [2]. However, variation in complexity, geographic availability and seasonality of biomasses, and respective characteristics poses huge challenges to the conception and assessment of proposed or and management of running biorefinery installations.

Indeed, the nature and properties of biomasses are of critical importance in the selection of the processing technologies, particularly for its use as fuel. Depending on the nature of biomasses, biofuels and biorefineries may be classified as first generation, if the use of its biomass raw material competes in any form with food or feed production, including land occupation. Second generation biofuels and biorefineries use lignocellulosic, particularly residual, biomasses as raw materials. Third generation biofuels and biorefineries applies algae as starting materials [1]. In terms of processing technologies those installations may be classified in thermal, chemical, or biochemical “platforms”.

Option for one or more of these platforms depends undoubtedly on the final main products to be obtained, but also on the characteristics of raw biomasses. Evidently a deep knowledge of the starting material, as detailed as possible, particularly, information on the ultimate or elemental analysis may be helpful in conception and implementation of conversion scheme. However ultimate analysis requires expensive equipment and may be frustrating and inefficient [3]. On the other hand, the so-called proximate analysis, i.e., the characterization of biomasses based on its water, fixed carbon, volatile matter, and ashes contents requires less expensive equipment and, therefore, is widely used by researchers in various modelling and prediction studies, also for process designing proposes. For instance, proximate analysis was extensively used to predict higher heating value (HHV), an extremely important parameter for the characterization of fuels, showing that it is a reasonable alternative to ultimate analysis [3].

In this context the classification of biomasses based on machine learning approaches and using proximate analysis data may be helpful in the decision-making process on and management of biorefinery or biofuels producing units. In this work, the methodologies and results for the identification of biofuels from their fixed carbon, volatile matter, and ashes contents using machine learning is presented.

2 Methods

In this section the dataset used is presented, along with the methods used to deal with the unbalanced nature of the data, and the methodology used to train and evaluate the classification models.

2.1 Data

The public dataset presented in [4] was used to build classification models to predict the solid biofuel type from their fixed carbon, volatile matter, and ash contents. The dataset was built from raw fuel composition data presented in a number of scientific publications

that were categorized as four different types of solid biofuels: coals, woods, agriculture residues, and manufactured biomass. The raw fuel elements categorized in each class are presented in Table 1.

Table 1. Categorization of raw fuels. From [4].

Class name	Raw fuels
Coals	Coals, charcoals, chars
Woods	Woods, shell, pruning
Agriculture Residues	Seed, husk, leaves, grass, bark, straw, stalk
Manufactured Biomass	Municipal solid waste, RDF, sludge, briquettes

The dataset comprises a total of 585 samples, with unequal distribution among the four classes of biofuels, as represented in Fig. 1.

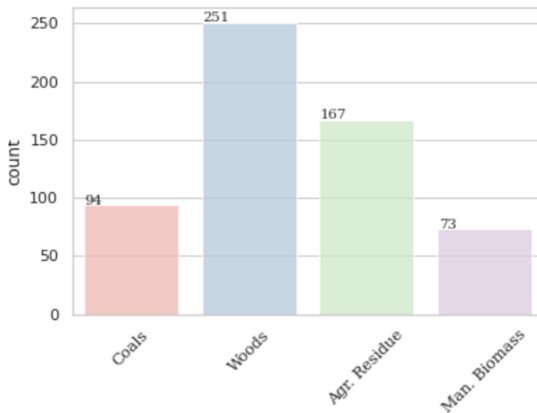


Fig. 1. Distribution of the dataset samples among the four solid biofuel classes.

The features available in the dataset for each sample are the contents of fixed carbon, volatile matter, and ash. The kernel density estimate (kde) plots presented in Fig. 2 show the distribution of the contents according to the biofuel class.

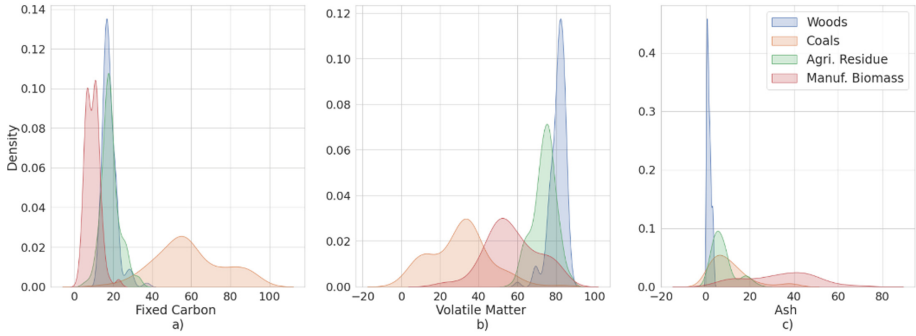


Fig. 2. Density plots for a) Fixed Carbon content, b) Volatile Matter content and c) Ash content. Different colors represent the different biofuel classes.

The kde plots show that both Manufactured Biomasses and Coals present to the naked eye with a good degree of separability from the other contents at least for one of the features, while Woods and Agriculture Residues are mostly overlapping.

The goal is to build classification models that allow to identify the biofuel category of the samples from the three mentioned features. Additionally, there is an appreciable degree of data unbalance, where the most represented class (Woods) represents 43% of the samples, whereas the less represented class (Manufactured Biomass) represents only 12% of the samples.

2.2 Data Sampling

The fact that the dataset presents an appreciable degree of class imbalance might constitute a challenge to the classification task. This happens because the machine learning models will tend to be more biased towards the majority class (or classes), and perform worse for the minority class (or classes) [5].

There are two main approaches to deal with the issue of data unbalance at the data level: either under-sampling or over-sampling. Under-sampling techniques, where some data are eliminated from the majority classes, have the disadvantage of reducing the size of the dataset. Over-sampling techniques can be used by generating new synthetic data. This was the approach followed in this work, where the SMOTE – Synthetic minority over-sampling technique [6] was used. For synthesizing new samples, the SMOTE algorithm starts by identifying neighbor examples from the minority classes in the feature space and then synthesizes a new example in the space between those neighbors. It repeats this procedure as many times as needed to create a balance between the number of samples in the classes.

In this work, the SMOTE implementation available at the *imbalanced-learn* module in the *scikit-learn* library [7] was used, which allows dealing with multiple minority classes, such as the present case.

2.3 Classification Models

Six different classification algorithms were chosen to train the classifiers: Logistic Regression(LR) [8] and Support Vector Machines (SVM) [9] were chosen due to their simplicity, ease to tune, and difficulty to overfit; Decision Trees (DT) [10] model was used because it provides more complex models, although at the expense of a tendency to overfit; Random Forests (RF) [11] and Extreme Gradient Boosting (XGB) [12], two ensemble techniques, although more difficult to tune, usually provide good performance models that are less likely to overfit than Decision Trees. To train these models the implementations available at the Scikit-learn library in Python [13] were used.

2.4 Model Training, Evaluation Metrics

Following the usual procedure, data were divided into a training set (80% of the samples) and a test set (20% of the samples). Then, for each model, a 5-fold cross validation procedure was used to avoid overfitting. This means that the training data set was divided into 5 blocks, and the training of each model was done with 4 of the blocks, with the remaining one being used for validation purposes. The process was repeated 5 times, once for each block, thus enabling the maximization of the total number of observations used for validation. The best average cross-validation estimator score was elected. Then, the overall performance of each elected model was assessed with the test set.

Accuracy (Eq. 1) is the global metric often used for evaluating classification models, computed as the number of correct predictions divided by the total number of predictions. It might however become an unreliable metric in the case of unbalanced data. In such cases, single class metrics are more adequate [14], since they allow for a better understanding of how the models behave for each class. In this work the f1-score (Eq. 4) is used, which accounts for the trade-off between precision (Eq. 2) and recall (Eq. 4), which also represent single class metrics.

$$Accuracy = \frac{TP + TN}{TP + TN + FP + FN} \quad (1)$$

$$Precision = \frac{TP}{TP + FP} \quad (2)$$

$$Recall = \frac{TP}{TP + FN} \quad (3)$$

$$f1 - score = 2 * \frac{Precision * Recall}{Precision + Recall} \quad (4)$$

For each trained model, f1-score, precision and recall were computed for each class, as well as the accuracy, and the average-f1 score.

In the previous equations, TP stands for True Positive, TN for True Negative, FP for False Positive, and FN for False Negative. For each model, these values were also plotted in a confusion matrix, a table that summarizes the performance of the classification model for each class.

For each trained model, f1-score, precision, and recall were computed for each class, as well as the accuracy, and the average f1-score.

3 Results

The confusion matrices obtained for each of the trained models are presented in Fig. 3. The dark green values along the main diagonal represent the percentage of True Positive values for each class. For each row, the values outside the diagonal represent the percentage of False Negative values for the respective class; for each column, the values outside the diagonal represent the percentage of False Positive values for the respective class.

From these matrices, it's possible to identify that both Coals and Woods are easier to correctly classify, regardless of the classifier used, than the other two biofuel classes. Coals is also one of the minority classes. The fact that every classification model presents high f1-score for this class is an indication that the data sampling technique achieved its goals. Agricultural Residues are often misclassified as Woods, which was expectable, given their content superposition, and also misclassified as Manufactured Biomasses. On the other hand, Manufactured Biomasses can be misclassified as Agriculture Residues.

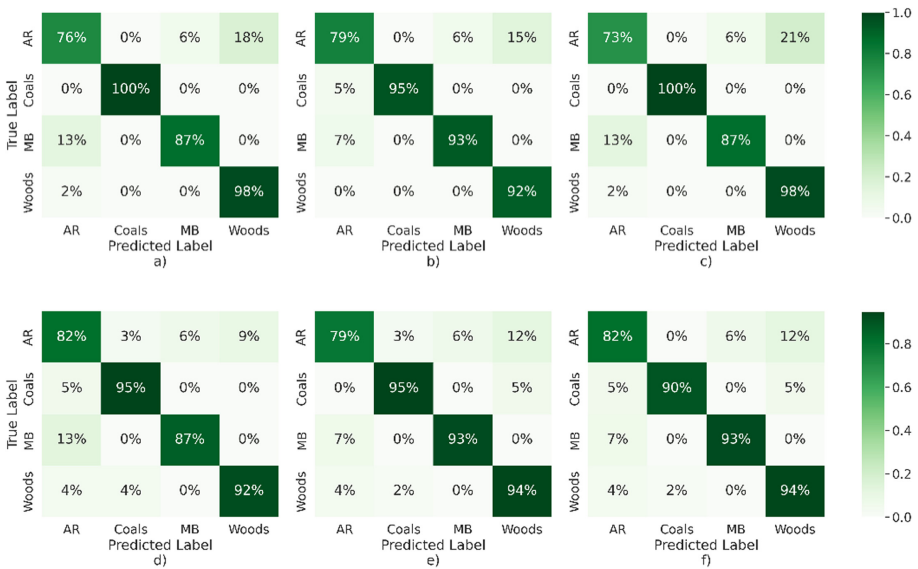


Fig. 3. Confusion matrix for the models a) Logistic Regression; b) k-Nearest Neighbors; c) Support Vector Machines; d) Decision Tree; e) Random Forest; e) Extreme Gradient Boosting.

The values for f1-score obtained with the six classification models for each class are presented in Table 2.

The f1-score values for the individual classes confirm that, in general, all models classify Coals and Woods with high f1-score (above 0.91), and that Agricultural Residues and Manufactured Biomasses seem to be harder to correctly classify, with lower f1-scores for those classes (below 0.91).

Finally, Table 3 presents the global metrics obtained for each of the trained models: accuracy, and the average values of f1-score, precision and recall.

Table 2. f1-score values for the individual classes, for the several trained models.

Biofuel class	LR	kNN	SVM	DT	RF	XGB
AR	0.82	0.80	0.80	0.83	0.84	0.84
Coals	1.00	0.97	1.00	0.90	0.93	0.92
MB	0.87	0.90	0.87	0.87	0.90	0.90
Woods	0.93	0.91	0.92	0.93	0.92	0.92

Table 3. Global metrics obtained with the trained models: average f1-score, average precision, average recall, and accuracy.

Model	f1-score	Precision	Recall	Accuracy
Logistic Regression	0.89	0.89	0.88	0.87
k-Nearest Neighbors	0.90	0.90	0.90	0.89
Support Vector Machines	0.88	0.89	0.88	0.88
Decision Tree	0.84	0.89	0.83	0.86
Random Forest	0.90	0.90	0.90	0.90
Extreme Gradient Boosting	0.90	0.90	0.90	0.90

Among the six trained classifiers, Random Forest and Extreme Gradient Boosting stand with the highest performance metrics, followed by the kNN model.

4 Discussion

In this work, a public dataset was used to build six classification models to predict the type of biofuel. The problem is addressed as a four-category classification task, in which there's an imbalance towards two of the classes. The SMOTE algorithm is used to promote class balancing with synthetic oversampling and six machine learning classification models are trained. The results show that both Random Forest and Extreme Gradient Boosting have the highest classification accuracy and that the Agriculture Residues is the biofuel type that is harder to correctly identify.

References

1. Cherubini, F.: The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manag.* **51**, 1412–1421 (2010). <https://doi.org/10.1016/j.enconman.2010.01.015>
2. Irena: BOOSTING BIOFUELS Sustainable Paths to Greater Energy Security Acknowledgements (2016)
3. Elmaz, F., Yücel, Ö.: Data-driven identification and model predictive control of biomass gasification process for maximum energy production. *Energy* **195** (2020). <https://doi.org/10.1016/j.energy.2020.117037>

4. Elmaz, F., Büyükçakır, B., Yücel, Ö., Mutlu, A.Y.: Classification of solid fuels with machine learning. *Fuel* 266 (2020). <https://doi.org/10.1016/j.fuel.2020.117066>
5. Ali, A., Shamsuddin, S.M., Ralescu, A.L.: Classification with class imbalance problem: a review. *Int. J. Adv. Soft Comput. its Appl.* 7, 176–204 (2015)
6. Chawla, N.V., Bowyer, K.W., Hall, L.O., Kegelmeyer, W.P.: SMOTE: synthetic minority over-sampling technique. *J. Artif. Intell. Res.* 16, 321–357 (2002). <https://doi.org/10.1613/jair.953>
7. Lema, G., Nogueira, F., Aridas, C.K.: Imbalanced-learn: a python toolbox to tackle the curse of imbalanced datasets in machine learning. *J. Mach. Learn. Res.* 40, 1–5 (2015)
8. Hastie, T.J., Pregibon, D.: Generalized linear models. In: *Statistical Models in S* (2017)
9. Cortes, C., Vapnik, V.: Support-Vector Networks. *Mach. Learn.* 20, 273–297 (1995). <https://doi.org/10.1111/j.1747-0285.2009.00840.x>
10. Quinlan, J.R.: Induction of decision trees. *Mach. Learn.* 1, 81–106 (1986). <https://doi.org/10.1007/bf00116251>
11. Breiman, L.: Random forests. *Random For.* 45, 5–32 (2001). <https://doi.org/10.1201/9780367816377-11>
12. Chen, T., Guestrin, C.: XGBoost: a scalable tree boosting system. In: *Proceedings of the ACM SIGKDD International Conference on Knowledge Discovery and Data Mining* (2016)
13. Pedregosa, F., et al.: Scikit-learn: machine learning in python. *J. Mach. Learn. Res.* 85, 2825 (2011)
14. Tanha, J., Abdi, Y., Samadi, N., Razzaghi, N., Asadpour, M.: Boosting methods for multi-class imbalanced data classification: an experimental review. *Journal of Big Data* 7(1), 1–47 (2020). <https://doi.org/10.1186/s40537-020-00349-y>



The Use of Infrared Thermographic Technique for the Detection of Energy Losses

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Abstract. The present study shows a research work on the use of infrared thermographic technique as a non-destructive tool for the inspection of energy losses in various installations. Infrared thermography is a method showing thermal images of areas where local changes of temperature indicate hidden structures of thermal patterns. The detection of different temperatures of industrial installations can be found easily by this technique. The influence of humidity on thermal behavior of materials is also can be analyzed. Ventilating and air conditioning applications also need thermography applications for its compartment evaluation and the detection of thermal patterns of different systems. Several experiments have been carried out using thermography technique for thermal drying process of different biomass residues. Also experiments of the detection of high temperatures of electrical installations of industrial systems have been realized. The results obtained indicate that temperature profile is an important parameter for the detection of anomalies for different processes.

Keywords: Energy losses · Infrared thermography · Temperature

1 Introduction

Infrared thermography is a very useful method showing thermal images of areas where local changes of temperature indicate hidden structures of thermal patterns of large walls, construction materials, biomass residues, etc. The temperatures indicate the state of these materials, and it will be easy to predict anomalies, as studied by Al-Kassir et al. [1, 2]. The environmental interest of biomass is due to the fact that this is the unique energy source that leads to a favorable CO₂ balance since the organic matter is able to retain more CO₂ than that released by its combustion. The transformation processes of biomass prior to be used as energy source may be classified as; physical processes – such as grinding and drying-, biochemical processes -such as alcoholic fermentation and anaerobic digestion, and thermochemical processes that yield to carbon, liquid hydrocarbons and gases. In order to increase the energy efficiency, improvement of energy production quality and reduction of emissions during energy conversion, biomass residues must be dried

commonly in industry via rotary dryers and screw dryers. In these dryers the biomass residues are fed from one side of the dryer cylinder and creates a loosely compacted bed in the screw that lets hot air pass through the bed of biomass residues and dries them. Drying time can be controlled by controlling the rotation speed of the screw [3].

2 Experimental Research

Several experiments have been carried out using thermography technique for thermal drying process of different biomass residues. Also experiments of the detection of high temperatures of electrical installations of industrial systems have been realized. Figure 1 shows the real image and the thermogram of the dryer.

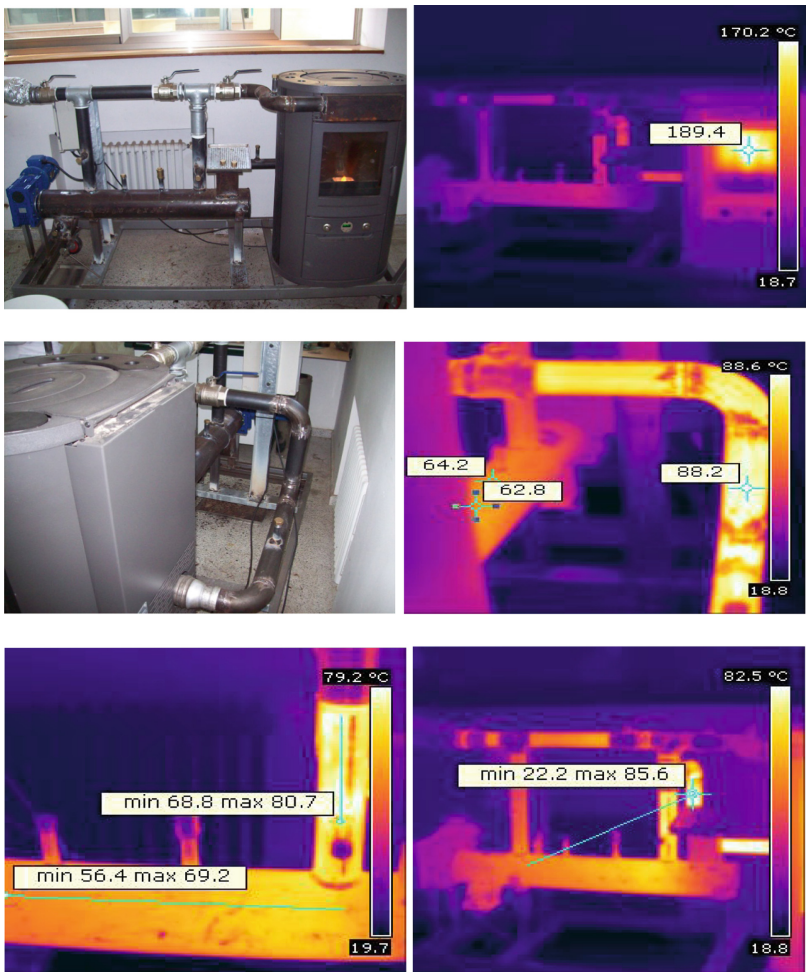


Fig. 1. Images and thermograms of the dryer.

Other experiments have been done on the detection of anomalies of photovoltaic solar panels. Figure 2 shows two panels inspected that have an anomalous square with high temperature.

Figure 3 shows the temperature profile of several experiments that have been realized during a study of the optimum indoor conditions of a meat factory in Spain. The temperature has been measured by using an infrared thermography camera. The results showed that the temperature inside the refrigerating space was correct.

Figure 4 indicates the normal operation of the electrical installation that have been inspected in the present study.

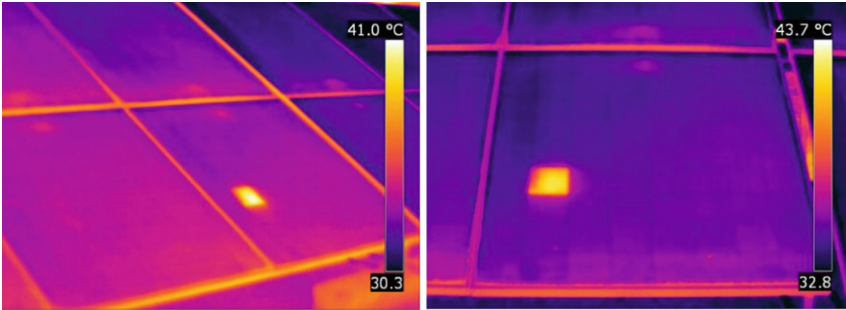


Fig. 2. Thermograms of the photovoltaic solar panels.

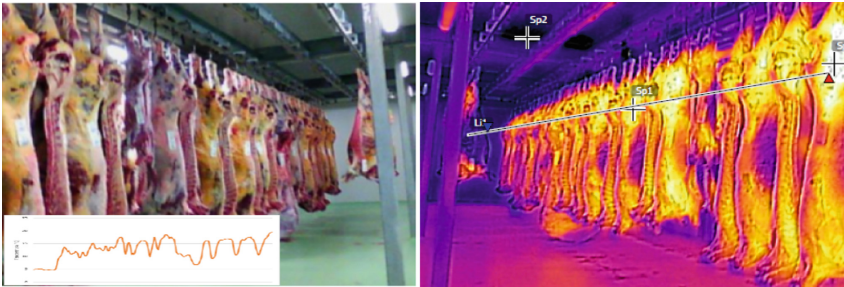


Fig. 3. Image and thermogram of the meat with temperature profile.

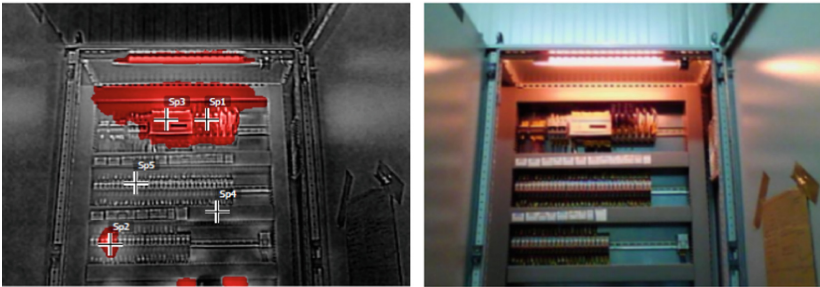


Fig. 4. Image and thermogram of electrical installations.

The heat loss of an exterior enclosure can be seen in Fig. 5. It indicates the areas of light color showing heat losses from the wall.

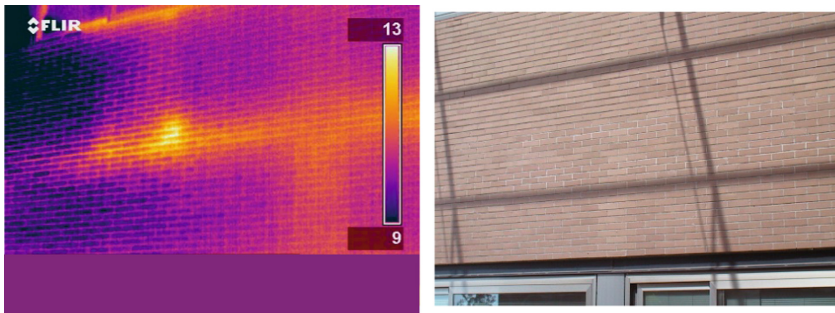


Fig. 5. Image and thermogram of an exterior enclosure.

Figure 6 depicts a thermographic image with the photograph of the false ceiling of the laboratory of our school of Engineering. A clear area is seen indicating the heat loss of the insulation of the roof however nothing is seen in the thermography corresponding to the same image.

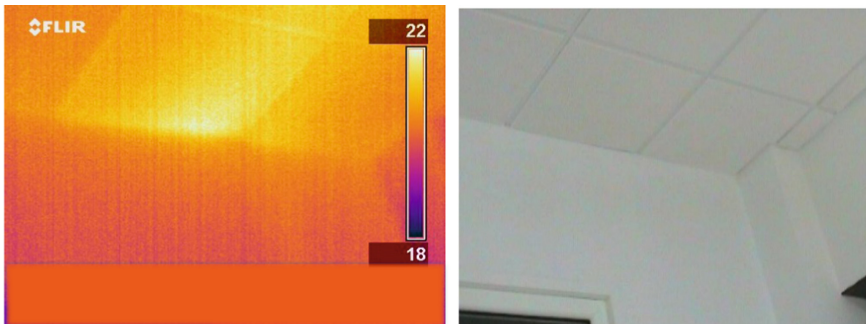


Fig. 6. Image and thermogram of a false ceiling.

3 Results

The results obtained from the drying experiments of residues showed a high reduction of moisture content after the fourth drying process. Figure 7 shows the temperature profile along the dryer for parallel flow between hot gas and woodchips at different temperatures of hot gas.

The other experiment realized on the solar panels shows the utility of the thermography technique for the detection of anomalies in energetic installations. The results obtained from the experiments realized on measuring meat temperature show the optimum indoor conditions of conservation of food and meat.

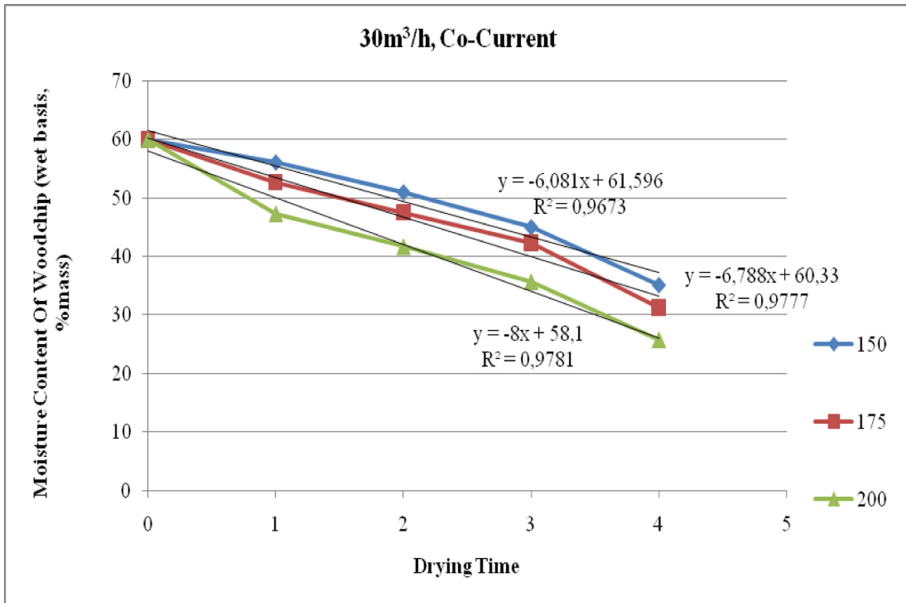


Fig. 7. Temperature profile along the dryer for parallel flow between hot gas and woodchips at different temperatures of hot gas.

4 Conclusions

The experimental work of the use of thermography technique has shown the useful application of the infrared radiation for the detection of anomalies of thermal and electrical systems.

The use of thermography in thermal drying process indicates that woodchips and olive pomace have been dried at different gas temperatures, then the reduction of humidity was achieved.

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References

- Al-Kassir, A., Ramiro, A., Castro, F., Tinaut, F.V.: Application of Infrared Thermography Technique on the Analysis of Monuments Construction, Thermal Systems and Electrical Installations. In” Managing Enterprises— Stakeholders, Engineering, Logistics, and Achievement, MEP, UK, pp. 375–380 (1997)
- Al-Kassir, A., Ramiro, A., Corchado, S.: Inspección mediante la técnica de termografía infrarroja de instalaciones eléctricas, MONTAJES E INSTALACIONES, October, pp. 85–89 (1997)
- Al-Kassir, A., Gañán, J., Tinaut, F.: Thermal drying. Appl. Therm. Eng. **25**, 2816–2826 (2005)



Biolubricant Production from Vegetable Oils Through Double Transesterification: Influence of Fatty Acid Composition and Alcohol on Quality Parameters

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Abstract. Biolubricants might represent an alternative for lubricants obtained from fossil fuels, presenting many advantages such as sustainability, environment-friendly characteristics or higher flash and combustion points (implying safety during storage or shipping). One way to produce biolubricants is through double transesterification of vegetable oils with different alcohols, obtaining interesting intermediate products such as fatty acid methyl esters, glycerol, or methanol (which can be re-used in the process). Thus, this procedure might be suitable for biorefinery implementation, promoting many of the sustainable development goals established by the UN. This way, the main quality parameters of a biolubricant (mainly oxidative stability and viscosity) are dependent on two main factors, that is, the raw material used (for instance, vegetable oils) and the alcohols applied (methanol or ethanol for the first transesterification and superior alcohols for the second transesterification). The aim of this work was to assess quality parameters (oxidative stability and viscosity, among others) in biolubricants obtained from different raw materials (cardoos, waste cooking oil, rapeseed and safflower oils) through double transesterification with different superior alcohols (pentaerythritol, 2-ethyl-2-hydroxymethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol). As a conclusion, raw material seemed to have a strong influence on oxidative stability, with higher oleic acid content promoting higher oxidative stabilities (up to 6 h), whereas the superior alcohol influenced on viscosity (ranging from 20 to 80 cSt), depending on the complexity of the alcohol used. Consequently, the selection of the right vegetable oil and alcohol is crucial to produce a biolubricant for a certain industrial use.

Keywords: Rapeseed · Safflower · Cardoon · Waste cooking oil · Pentaerythritol · 2-ethyl-2-hydroxymethyl-1,3-propanediol · 2,2-dimethyl-1,3-propanediol

1 Introduction

Due to the current scenario, implying an increasing concern about sustainability and environmental aspects, many agencies, organizations, and governments are promoting sustainable processes, paying attention to green chemistry and circular economy. In fact, and on account of the current geopolitical situation, where energy and fuel supply are vital, a renewed search for alternatives in order to reduce the dependence on natural gas or petroleum-based fuels has emerged [1].

This way, the implementation of biorefineries, where natural raw materials are used in order to produce bioproducts (and by-products that can be re-used in the process) could be a suitable way to meet current environmental challenges. For instance, in this present work, the production of biolubricant from vegetable oils is an example of biorefinery, with several advantages such as the use of natural (and local) raw materials and production of biodegradable products (which makes the process environmentally friendly), promoting sustainable and local economic development [2].

In that sense, some of the characteristics of a biorefinery (based on vegetable oils, in this case) could be within the framework established by the Sustainable Development Goals (SDG), supported by the United Nations. For instance, SDG related to “Affordable and clean energy”, “Decent work and economic growth” or “Climate action”, among others, could fit in a biorefinery context [3].

Regarding biolubricants, they can act as a replacement for lubricants based on petrochemical products. As observed in Fig. 1, there has been a considerable increase in lubricant demand in the last decade, mainly due to the increase in global industrial activity. As a consequence, the market for biolubricants could be promising [4].

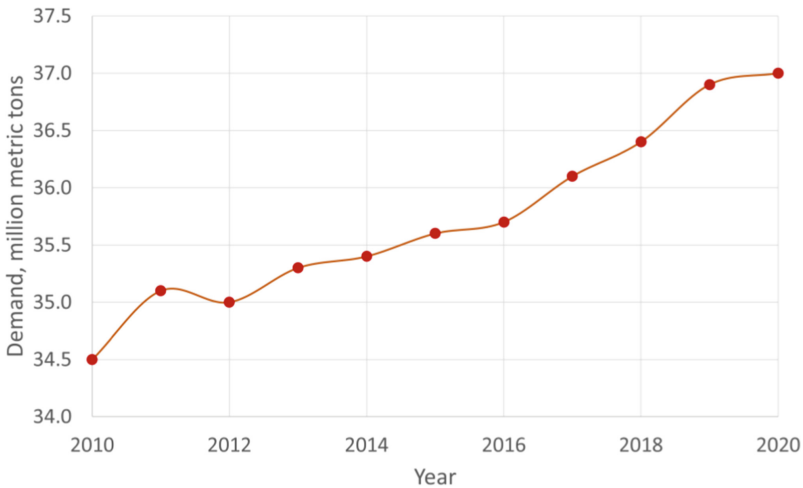


Fig. 1. Biolubricant demand evolution [5].

Paying attention to global production of lubricants (see Fig. 2), some regions (Asia-Pacific and North America) seem to produce almost 75% of lubricants. In that sense, the

implementation of biorefineries based on biolubricant production could be an important opportunity for Europe, in order to improve its productivity in a sustainable way. Thus, some European regions, like those with a long-established agricultural culture, could benefit from this scenario, with the subsequent economic growth through green chemistry and circular economy.

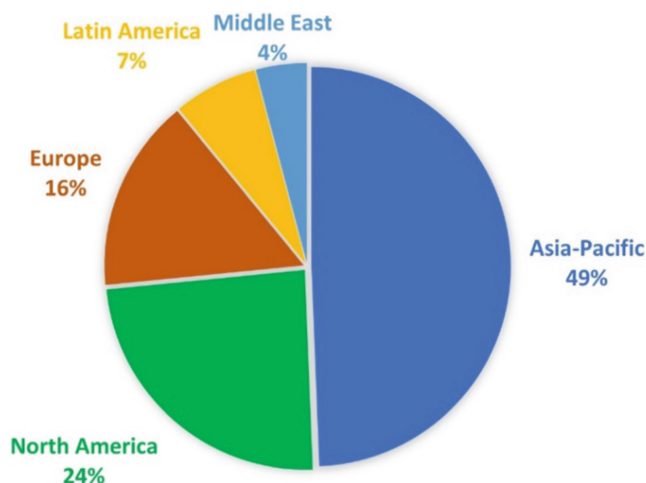


Fig. 2. Biolubricant demand by regions [5].

Apart from the evident environmental advantages (such as biodegradability), the use of biolubricants present other additional benefits like higher flash and combustion points (which make them safer during storage or shipment) or higher viscosity index (that is, lower changes in viscosity with temperature, which is important to assure a specific use of biolubricants for a certain industry at a specific temperature range) [4].

However, some challenges are related to biolubricants, like their usual low oxidative stability, which makes them unstable during storage. Specifically, auto-oxidation processes can take place in biolubricants, due to the presence of functional groups such as double bonds, which can generate free radicals (initiation stage).

As a consequence, propagation and termination stages take place in biolubricants, generating polymerization and free-fatty acids and increasing their viscosity and acid number during storage. Consequently, the properties of biolubricants might vary, and its quality can be compromised [4, 6].

The oxidative stability of a certain biolubricant can be influenced by many factors, such as storage conditions (temperature and contact with air), fatty acid composition of the raw material (some fatty acids are more stable than others, depending on their molecular structure), production method (the use of different kinds of alcohol can produce different complex molecules) or the use of antioxidants (which can increase the oxidative stability of products like biodiesel or biolubricants) [7, 8].

Considering the above, the aim of this work was to produce different biolubricants from several vegetable oils and superior alcohols, in order to compare their oxidative stabilities and assess the influence of the raw material or the kind of alcohol on this quality parameter.

2 Materials and Methods

2.1 Raw Materials

The raw materials used in this study were different vegetable oils: cardoon, waste cooking, rapeseed and high-oleic safflower oils. All the samples, except for waste cooking oil (which was provided by local restaurants and homes in Badajoz), were provided by the “Agrarian Research Institute Finca la Orden-Valdesequera, from CICYTEX, Centro de Investigaciones Científicas. Seed oil was extracted through mechanical methods, filtering all the samples before storage in opaque bottles at room temperature.

2.2 Transesterification Reaction for Biodiesel and Biolubricant Production

Biodiesel and biolubricant production were carried out through double transesterification. Thus, the first stage was fatty acid methyl ester (FAME) production in a batch reactor, by using the corresponding vegetable oil and methanol (6:1 methanol:oil ratio) and catalyst (MeONa, 0.5% w/w), at 65 °C during 90 min. Different purification processes (glycerol removal, washing treatments and drying) were carried out in order to obtain the final sample.

For biolubricant production, a similar procedure was carried out, and the reaction between the biodiesel obtained in the previous stage and the corresponding superior alcohol (2-ethyl-1-hexanol, 2,2-dimethyl-1,3-propanediol, trimethylolpropane or pentaerythritol) at different temperature ranges (between 120 and 160 °C), with catalyst addition (MeONa, 0.75% w/w) and vacuum, if necessary, during 120 min, as explained elsewhere [7–9]. Once the reaction took place, the sample was purified through vacuum filtration, being stored in opaque bottles at room temperature for further studies.

2.3 Biodiesel and Biolubricant Characterization

For biodiesel and biolubricant characterization, the main parameters included in UNE-EN 14214 standard were measured [10]. In that sense, viscosity at 40 °C and oxidative stability were measured according to previous studies by using a viscosimeter and the Rancimat method, respectively [7, 11].

To sum up, Fig. 3 shows the main steps followed in this experimental design.

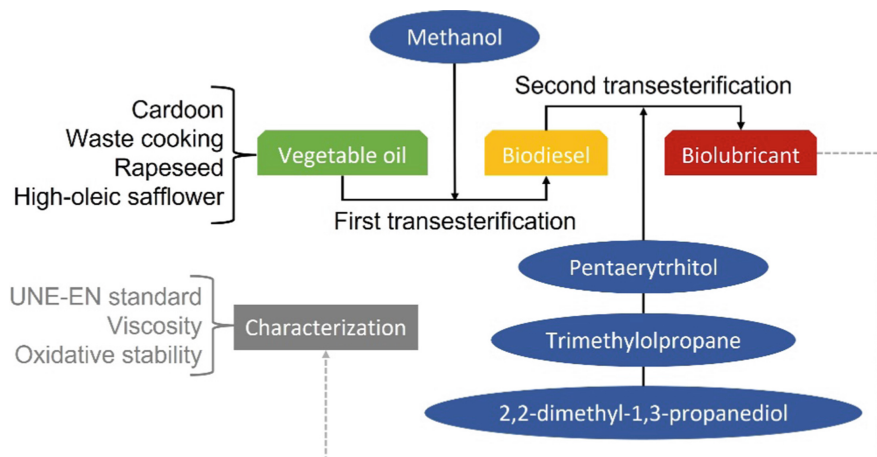


Fig. 3. Experimental design.

3 Results and Discussion

3.1 Biodiesel Characterization

As it can be seen in Table 1, most properties were similar among the different biodiesel samples, complying with the standard UNE-EN 14214 [10]. For instance, their safety during storage (flash point) was higher compared to conventional diesel, and high yields were obtained, assuring at least 96.5% of fatty acid methyl esters.

However, the oxidative stability of biodiesel was different depending on the raw material used, not complying with the standard for cardoon, waste cooking and rapeseed oil. In these cases, some solutions are proposed, such as antioxidant addition [12, 13]. In that sense, the use of tert-butylhydroquinone (TBHQ) was proved as an interesting

Table 1. Biodiesel characterization.

Parameter	Cardoon	Waste cooking	Rapeseed	High-oleic safflower	UNE-EN 14214
Yield, %	96.72	96.88	96.69	97.22	96.50
Viscosity at 40 °C, cSt	4.62	4.52	4.89	4.50	3.505.00
Density at 15 °C, kg·m ⁻³	879	865	850	872	860900
Oxidative stability, h	2.29	2.55	5.88	8.19	8.00
Flash point, °C	178	182	183	190	120
Acid value, mg KOH·g ⁻¹	0.28	0.39	0.31	0.18	0.50

additive to improve the oxidative stability in biodiesel. On the other hand, high-oleic safflower presented values above 8h, complying with the standard without requiring any antioxidant addition.

This fact could be explained by their fatty acid methyl ester profile, as included in Fig. 4. This way, methyl oleate content in biodiesel samples increased in this order: cardoon (55%), waste cooking (56%), rapeseed (65%) and high-oleic safflower (82%). On the contrary, methyl linoleate content decreased in this order: waste cooking (29%), cardoon (25%), rapeseed (18.2%) and high-oleic safflower (9.3%).

As these two fatty acid methyl esters were the majority compounds in these biodiesel samples, they had a strong influence on oxidative stability. Thus, methyl oleate, which is mono-unsaturated, is more stable than methyl linoleate, with two unsaturations points has lower oxidative stability. This is due to the fact that unsaturations are prone to generate free radicals, promoting the initiation stage during auto-oxidation [14].

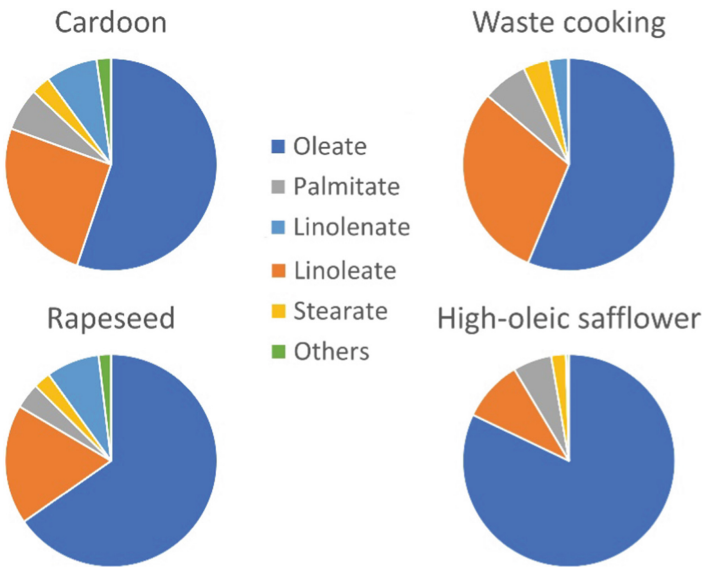


Fig. 4. FAME profile of different biodiesel samples.

As a consequence, cardoon and waste cooking biodiesel presented short oxidative stabilities (below 3 h), whereas rapeseed and, especially, high-oleic safflower (with a high methyl oleate/linoleate ratio) had longer induction periods (around 6 and exceeding 8 h, respectively). This way, the influence of the original fatty acid composition, which is completely transformed into the corresponding fatty acid methyl esters, is vital to understand some quality parameters in biodiesel, as in the case of oxidative stability [15].

3.2 Influence of Fatty Acid Composition on Biolubricants

As compared in the preceding section, fatty acid profile of the corresponding raw material can play an important role in some quality parameters in biodiesel and, according to Table 2, in biolubricants.

Table 2. Oxidative stability (in h) for different biolubricants.

Alcohol used	Cardoon	Waste cooking	Rapeseed	High-oleic safflower
2-ethyl-1-hexanol	2.21	2.45	6.02	7.32
2,2-dimethyl-1,3-propanediol	2.36	3.02	5.56	6.82
Trimethylolpropane	2.42	3.69	4.94	6.52
Pentaerythritol	2.06	2.14	2.39	2.92

As inferred from this table, there were clear differences in oxidative stability depending on the kind of oil. Thus, as it happened in the case of biodiesel, a higher content in oleic acid (and subsequently methyl oleate for biodiesel or the corresponding oleate for the biolubricant) seemed to assure longer oxidative stability, as in the case of high-oleic safflower biolubricant. This could be due to the presence of more stable esters, mono-unsaturated, compared to the di- or poly-unsaturated esters produced by linoleic or linolenic acids [15]. Additionally, the different alcohols used could affect the oxidative stability of the final biolubricant. Thus, the presence of a higher number of hydroxyl groups in the alcohol allowed to synthesize more complex esters, which would be, in general, less stable (implying shorter oxidative stability values). This could be the reason why, compared to fatty acid methyl esters, all the biolubricants covered in this study were less stable.

3.3 Influence of the Alcohol Used for Biolubricant Production

The main chemical reactions that took place during the second transesterification of fatty acid methyl esters (biodiesel) to produce the corresponding alcohol are included in Fig. 5.

In that sense, fatty acid methyl esters (e) reacted with the corresponding hydroxyl group in the alcohol, obtaining different molecules with an increasing complexity when the alcohol presented an increasing number of hydroxyl groups.

Thus, alcohol (a) presented one single hydroxyl group, whereas alcohols (b, c and d) had 2, 3 and 4 hydroxyl groups, respectively. Taking into account that conversions in all cases exceeded 90%, it was assumed that all -OH groups reacted with FAMES, obtaining complex esters (biolubricants) with increasing complexity: $a < b < c < d$, in that order.

Depending on the alcohol used, differences in viscosity values were observed, as it can be inferred from Table 3. This way, as the complexity of the alcohol increased (from

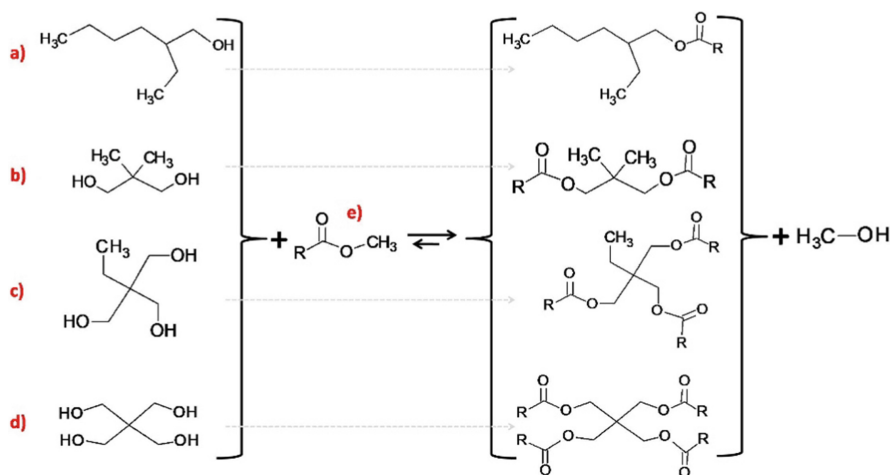


Fig. 5. Second transesterification with different alcohols: a) 2-ethyl-1-hexanol; b) 2,2,-dimethyl-1,3-propanediol; c) trimethylolpropane; d) pentaerythritol. All the reactions were carried out with fatty acid methyl esters (e).

2-ethyl-1-hexanol to pentaerythritol), the viscosity of the final product was higher. This could be due to the fact that, as the biolubricant was more complex, it could present additional molecular branches, which can interact through intermolecular bonds such as hydrogen bonds and, subsequently, present higher resistance to flow [11].

Table 3. Viscosity at 40 °C (in cSt) for different biolubricants.

Raw material (oil)	2-ethyl-1-hexanol	2,2-dimethyl-1,3-propanediol	Trimethylolpropane	Pentaerythritol
Cardoon	8.31	18.90	70.92	69.20
Waste cooking	7.52	18.47	71.85	70.18
Rapeseed	8.01	20.01	72.51	76.21
High-oleic safflower	7.93	19.72	71.92	77.72

Regarding the different raw materials used, there were no clear trends or differences among the samples, showing similar viscosity values for each kind of alcohol used.

4 Conclusions

The main findings of this research work were the following: a) biorefinery based on vegetable oil through double transesterification could be a suitable starting point for the

implementation of a biorefinery. b) Some quality parameters of the final biolubricant, through this production method, are highly influenced by the vegetable oil and alcohol used. c) Thus, the fatty acid profile of the vegetable oil had a strong influence on oxidative stability, showing that high levels of oleic acid could contribute to longer induction periods. d) finally, the alcohol used during the second transesterification mainly influenced the viscosity of the final biolubricant, making the selection of multiple complex alcohols vital for the diversification of a biorefinery based on vegetable oils.

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References

1. Sánchez-Carracedo, F., López, D., Martín, C., Vidal, E., Cabré, J., Climent, J.: The sustainability matrix: a tool for integrating and assessing sustainability in the bachelor and master theses of engineering degrees. *Sustain* **12**(14), 1–23 (2020)
2. Moncada, B.J., Aristizábal, M.V., Cardona, A.C.A.: Design strategies for sustainable biorefineries. *Biochem. Eng. J.* [Internet]. **116**, 122–134 (2016). <http://dx.doi.org/https://doi.org/10.1016/j.bej.2016.06.009>
3. United Nations. Transforming our world : the 2030 Agenda for Sustainable Development [Internet]. (2015). <https://www.un.org/sustainabledevelopment/sustainable-development-goals/>
4. McNutt, J., He, Q.S.: Development of biolubricants from vegetable oils via chemical modification. *J. Ind. Eng. Chem.* [Internet]. **36**, 1–12 (2016). <http://dx.doi.org/https://doi.org/10.1016/j.jiec.2016.02.008>
5. Statista. Global biolubricant demand [Internet]. (2022). <https://www.statista.com/statistics/411616/lubricants-demand-worldwide/>
6. Zhang, W., Ji, H., Song, Y., et al.: Green preparation of branched biolubricant by chemically modifying waste cooking oil with lipase and ionic liquid. *J. Clean. Prod.* [Internet]. **274**, 122918 (2020). <https://doi.org/10.1016/j.jclepro.2020.122918>
7. Encinar, J.M., Nogales-Delgado, S., Pinilla, A.: Biolubricant production through double transesterification: reactor design for the implementation of a biorefinery based on rapeseed. *Processes* **9**(7), 1224 (2021)
8. Encinar, J.M., Nogales, S., González, J.F.: Biodiesel and biolubricant production from different vegetable oils through transesterification. *Eng. Reports.* (January), 1–10 (2020)
9. Encinar, J.M., Nogales-Delgado, S., Sánchez, N., González, J.F.: Biolubricants from rapeseed and castor oil transesterification by using titanium isopropoxide as a catalyst: production and characterization. *Catalysts*. **10**(4) (2020)
10. UNE-EN 14214:2013 V2+A1:2018. Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods (2018)
11. Nogales-Delgado, S., Encinar Martín, J.M.: Cardoon biolubricant through double transesterification: assessment of its oxidative, thermal and storage stability. *Mater. Lett.* **302** (2021)

12. Nogales-Delgado, S., Encinar, J.M., Guiberteau, A., Márquez, S.: The effect of antioxidants on corn and sunflower biodiesel properties under extreme oxidation conditions. *JAOCS, J. Am. Oil Chem. Soc.* (2019)
13. Nogales-Delgado, S., Guiberteau, A., Encinar, J.M.: Effect of tert-butylhydroquinone on biodiesel properties during extreme oxidation conditions. *Fuel* [Internet]. **310**(PB), 122339 (2022). <https://doi.org/10.1016/j.fuel.2021.122339>
14. Nogales-Delgado, S., Encinar, J.M., González, J.F.: Safflower biodiesel : improvement of its oxidative stability by using BHA and TBHQ. *Energies* **12**(10), 1940 (2019)
15. Nogales-Delgado, S., Encinar, J.M., González Cortés, Á.: High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production. *Ind. Crops Prod.* **170**, 113701 (2021)



Comparative Analysis of Inrush Current and Harmonic Generation in the Replacement of Incandescent Lamps by LED Luminaires in Urban Lighting

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Abstract. Currently, LED technology is an established form of lighting in our cities and homes due to its lighting performance, durability, energy efficiency and light, together with the economic savings compared to discharge luminaires. However some problems associated with the large-scale replacement of incandescent lamps by LED luminaires have begun to be detected, which end up affecting on the circuit to which the luminaires are connected and on various components such as wiring and protections. These problems include the heating of conductors and the breakdown of overcurrent protections.

The purpose of this paper is to study and compare the two key parameters in the above mentioned problems such as inrush current and harmonic generation in both street lighting luminaires. This two parameters will be studied and how they can be used to predict or estimate the wiring cross-section of the circuits or the number of adequate overcurrent protection mechanisms to be installed for proper replacement.

Keywords: LED · Discharge · Inrush current · Harmonic generation · Electrical consequences and urban lighting

1 Introduction

The term “power quality” refers to a series of electromagnetic phenomena existing in an electrical network that affects its voltage and current parameters: deviation from the ideal waveform (harmonics), appearance of a transient state (peak current at start-up), $\cos \varphi$, and symmetry [1].

Several studies reveal that harmonic generation and peak currents are the main problems and negative effects related to the power quality associated with electronic sources (drivers) of LED technology. The inrush values depend a lot on the exact moment in which the switching occurs, if this coincides with a peak of the waveform very high currents will be produced, if it coincides with a zero crossing will be the opposite. Given this situation, the need arises to know what type of technology produces higher inrush current during switching and this paper aims to answer this question [2]. Harmonic distortion is another electrical parameter that will be studied in the replacement of luminaires since LED lighting equipment generates a relatively high level of harmonic distortion in the current due to the nonlinear nature of LEDs. These phenomena, if not controlled, can reduce the lifetime of LED lighting and affect the lumen output and/or cause light flicker that can affect user comfort [3].

LED drivers are the most important component of this type of luminaires to improve the concept of “power quality”. Most of the drivers were based on switched-mode voltage converters, evolving towards new circuit typologies that can be used as current sources for LED applications [1].

2 Instrumentation and Methods

2.1 Instrumentation

A network analyzer (Fluke, Model: 437, Series II) was used to measure the electrical parameters and harmonics in the supply lines: voltage, inrush current, active power, reactive power, phase voltage and neutral conductor current harmonics. The Table 1 shows the main technical specifications of network analyzer.

Table 1. Table of specifications network analyzer.

Specification	Measurement range	Resolution	Precision
Peak Voltage	1V–1400 V	0,01 V	± 0,1%
Peak Current	5500 Ap	1A RMS	± 0,5%
Frequency	42,50 Hz69 Hz	0,01 Hz	± 0,01 Hz
Power factor	0–1	0,001	± 0,1%
THD (Total harmonics Distortion)	THD current	0,10%	± 2,5%
THD (Total harmonics Distortion)	THD voltage	0,10%	± 2,5%

The current probe used, together with the network analyzer, is the i430 Flexi-TF probe, whose technical characteristics are detailed in the following Table 2:

2.2 Method

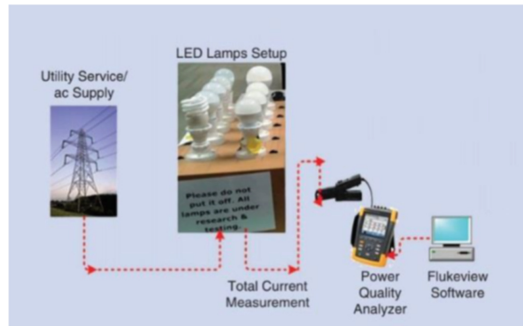
A simple methodology is proposed to detect and classify power signal disturbances of new LED lighting equipment, compared to LED technologies of different age and

Table 2. Table of specifications current probe.

Specification	Value
Current range	6000A CA RMS
Voltage Output (1000A RMS, 50 Hz)	86,6 mV
Precision	$\pm 1\%$
Output impedance	82 Ω
Load impedance	50 M Ω
Internal resistor	10,5 Ω
Bandwidth	10 Hz–7 kHz

discharge technologies, which can be important to the power quality of the installation [4]. The Fig. 1 details the laboratory set-up used to measure the following electrical parameters.

- Transient: inrush current
- Eventual: supply voltage variations
- Steady state: harmonics, fluctuations and frequency variations.

**Fig. 1.** Experimental set-up for the measurement of electrical parameters.

In the previous set-up, the luminaires under test will be supplied with single-phase mains voltage (230 V, 50 Hz), a Fluke network analyzer connected to them will be able to measure each of the most important electrical parameters, and using the own software we will save this data to be processed later and draw conclusions about the power quality of each of the luminaires under study.

A total of seven urban luminaires were analyzed, of which five corresponded to LED technology and two to discharge technology (Metal Halide and High Pressure Sodium Vapor).

The process followed in the investigation was as follows:

1. The study of electrical phenomena of the street lamps consisted of four days of analysis of each of the seven luminaires. Each day of analysis was structured in six measurement intervals for each luminaire. Within each measurement range, we distinguish between two types of start-ups that can exist in a luminaire:
 - a) **Cold start:** This is the name given to the type of start-up that takes place in luminaires after a long period of non-operation, normally this period of non-operation is usually several hours. It is considered that the cold start of a luminaire lasts until it reaches its permanent regime, as far as electrical phenomena are concerned.
 - b) **Warm start:** This is the name given to the type of start-up that takes place in luminaires after a short period of non-operation, normally this period of non-operation usually lasts for a few minutes. A warm start of the luminaire is considered to be the start-up of the luminaire when a short period of time has elapsed since the previous start-up.
2. The collected data were used to calculate statistics parameters for both technologies and then the results were compared. With this results, it was possible to evaluate the inrush current and harmonic generation in the circuit and finally draw conclusions from this study.

3 Equipment Under Test

The following Table 3 shows the technical characteristics of the seven urban luminaires that have been tested in this paper:

Table 3. Table of technical specifications urban luminaires.

Luminaire	Technology	Power	Input Voltage	Power factor	Lighting source
LEDUS LGLIAS	LED	60 W	AC 90-305 V	0,95	Philips-Lumileds
LEDUS LRLT1A	LED	80 W	AC 90-305 V	0,95	Philips-Lumileds
Philips Mini Iridium	LED	20 W	AC 220-240 V	0,95	Philips-Lumileds
NaviaP Solydi	LED	50 W	AC 100-300 V	0,95	CREE Xlamp XT-E
ATP Air 7	LED	200 W	AC 100-240 V	0,95	OSRAM LUW CQAR
High PSodium Vapor	Discharge	250 W	AC 100-240 V	0,97	SON-T E40 1SL
Metal Halide	Discharge	100 W	AC 100-240 V	0,97	CDO-TT Plus E40

4 Results and Discussion

The purpose of this study is to detect possible adverse electrical effects during nominal operation that may occur during both cold start and warm start and that may affect both the luminaires and the protection and control elements that make up the public lighting system (protection and ignition panels, power lines, etc.)

The first comparison to be made will be of the peak current in each type of ignition. We will compare the average values of the inrush current in each situation (cold start and warm start).

In addition, to calculate the severity of these inrush currents in each case, we will calculate a peak factor that symbolizes the number of times that the peak current exceeds the nominal RMS (Root Mean Square) value of the current consumption in each luminaire, and is defined as follows:

$$\text{Peakfactor} = \frac{\text{Inrushcurrent}}{I_{RMS}} \quad (1)$$

Comparison of average results show that the peak factor is higher in cold start than in warm start. It can be observed in the following Table 4:

Table 4. Average inrush current comparison.

Average inrush current (A)	Cold start	Warm start	I _{RMS} cold	I _{RMS} warm	Peak factor cold start	Peak factor warm start
LEDUS LGL1AS	2,73	3,12	0,23	0,27	12,1	11,5
LEDUS LRLT1A	3,55	3,07	0,30	0,30	11,8	10,2
Philips M-Irid	0,30	0,30	0,10	0,10	3	3
NaviaP Solydi	4,30	3,21	0,20	0,20	21,5	16
ATP Air 7	5,40	6,03	0,80	0,80	6,8	7,5
High P.S Vapor	6,65	5,54	1,43	1,37	4,6	4,0
Metal Halide	4,27	5,54	0,50	0,50	8,5	11,1

This comparison is very interesting since discharge lamps have hardly any electronic components or electronic sources that control the luminaire, so they do not have a large peak current [5] with respect to their nominal value in the electrical circuit as most LED luminaires do, as shown in Table 4.

The second and last comparison to be made will be of the total harmonic current distortion. The average values of harmonic generation produced by each luminaire and the difference between cold generation and hot generation will be checked, as shown in Table 5.

Table 5. Average total harmonic distortion (THD).

Average THD (%)	Cold start	Warm start
LEDUS LGL1AS	11,13	11,21
LEDUS LRLT1A	8,08	8,17
Philips M-Irid	13,90	14,52
NaviaP Solydi	13,50	13,76
ATP Air 7	6,10	6,22
High P.S Vapor	33	35,01
Metal Halide	10,23	10,19

Table 5 shows that for all luminaires, except for the MH discharge luminaire, the highest harmonic generation occurs in the warm start instead of the cold start, but with very small differences between cold THD and warm THD for all luminaires, which allows us to affirm that harmonic generation is independent of the type of luminaire ignition.

Finally, another interesting fact to observe in Table 5, the MH discharge lamp, despite of using discharge technology, behaves better harmonically than all the luminaires using LED technology, except for the ATP Air 7, which allows us to affirm that its starting ballast filters well the current harmonics produced during operation.

5 Conclusions

The disadvantage of switching to energy efficient luminaires such as LEDs is the increase in current THD [6, 7] and high peak currents at start-up [5].

The cold start for LEDs dangerously multiplies the nominal current. The cause could be that the driver capacitors are charged or discharged depending on the instant of start-up. The problem becomes even more obvious and more pronounced if we assume a real case of an ignition circuit consisting of, for example, 100 LED luminaires. If all of them are started at the same time, there is a risk that the overcurrent protection will automatically trip and prevent the system from switching on normally.

Two solutions are proposed for the cold start of LED luminaires, one of them very cheap as it has little impact in economic terms and the other more expensive as it involves a technological evolution of the driver: the first and cheapest solution to solve this problem is to synchronously start the various circuits of the electrical panel in order not to exceed the maximum current withstand by the circuit breakers, and the second and most expensive solution is to design a soft-start circuit in the drivers of the luminaires.

Analyzing the warm start, the most dangerous situation occurs when the luminaires start up with a maximum peak current, since the current multiplier factor is very high. This case is very common as it is caused by various factors such as a lightning strike, power failure, etc. A disconnection occurs and the panels with resettable devices would reconnect and now the danger is that these peak currents appear, as they could cause a second disconnection or a chain of disconnections that would prevent a normal ignition, then the applicable solutions, as we have explained above are the sectorized starting of each of the circuits or install a programmable driver in each of the luminaires to remedy these problems.

Regarding harmonic distortion, from the results of this study it can be concluded that the harmonic emission of LED lamps will be higher than that of incandescent lamps [8, 9, 10], which draw a current close to sinusoidal when fed by a sinusoidal voltage waveform. In addition, it has also been verified that in each of the luminaires there is practically the same harmonic distortion in both cold start and warm start, which allows us to affirm that the harmonic generation is independent of the type of start to which the luminaire is subjected and dependent on its electronic driver.

The high generation of harmonics is dangerous for the components that make up the system, as it can cause the conductors to heat up. To solve this problem, a driver capable of filtering the highest harmonics at the frequencies where they appear is proposed, with the disadvantage of increasing the price of the luminaire.

References

1. Hermoso Orzáez, M.J., Gago Calderón, A., Rojas-Sola, J.I.: Power quality and energy efficiency in the pre-evaluation of an outdoor lightning renewal with light-emitting diode technology: experimental study and amortization analysis. *Energies* 7 (2017). <https://doi.org/10.3390/en10070836>
2. Wu, C.N., Chen, Y.L., Chen, Y.M.: Primary-side peak current measurement strategy for high-precision constant output current control. *IEE Trans. Power Electronics* 2, 967–975 (2015). <https://doi.org/10.1109/TPEL.2014.2312955>
3. Gil-de-Castro, A., Moreno-Muñoz, A., Larsson, A., de la Rosa, J.J.G., Bollen, M.H.J.: LED Street lighting: a power quality comparison among street light technologies. *Light. Res. Technol.* 6, 710–728 (2013). <https://doi.org/10.1177/1477153512450866>
4. Verma, P., Patel, N., Nair, N.K.C.: Light-emitting diode electronics, harmonic issues, and augmenting standards. *IEEE Consumer Electronics Magazine* 6, 150–156 (2017). <https://doi.org/10.1109/MCE.2017.2714280>
5. Markiewicz, P., Sikora, R., Pabjanczyk, W.: Statistical analysis of peak inrush current: a case study. *Compel-the International Journal for Computation and Mathematics in Electrical and Electronic Eng.* 3, 1069–1084 (2018). <https://doi.org/10.1108/Compel-07-2017-0312>
6. Mohd, I., Noor, C., Abdul, S., Amith, K., Atif, I., Haitham, A.-R.: Power quality effect of using incandescent, fluorescent, CFL and LED lamps on utility grid. *IEEE Firts Workshop on SmartGrid and Renewable Energy (SGRE) I*, 1–5 (2015)
7. Pentiu, R.-D., Popa, C.-D., Dascalu, A., Atanosoa, P.: The influence of LED street lighting upon power quality in electrical networks. *International Conference and Exposition on Electrical and Power Engineering*, pp. 1092–1098 (2014)
8. Blanco, A.M., Stiegler, R., Meyer, J.: Power quality disturbances caused by modern lighting equipment (CFL and LED). In: 2013 IEEE Grenoble Conference PowerTech, POWERTECH 2013 (2013)

9. Uddin, S., Shareef, H., Mohamed, A., Hannan, M.A.: An analysis of harmonics from LED lamps, cccc2012 Asia-Pacific Symposium on Electromagnetic Compatibility. APEMC 2012—Proceedings, pp. 837–840 (2012)
10. Rehman, M.M.U., Shabbir, H., Rehman, S.A., Sheikh, S.K., Zaffar, N.: A comparative analysis of electrical and photo characteristics of LED lights. In: Proceedings—10th International Conference on Frontiers of Information Technology, FIT 2012, pp. 219–224 (2012)



Analysis of the Digestate Obtained in Experiences in a Pilot Plant in Extremadura and Study of the Possible Effect Produced as an Organic Fertilizer in Pepper Plants

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Abstract. Digestate from anaerobic digestion process can be apply as fertilizer in different crops and horticulture plants due to high amount organic matter content and nutrients variability. Tests carried out to study the digestate as organic fertilizer were developed with pepper plants where the plant growth, and fruit, plant, soil and root composition were evaluated. Three treatments were developed evaluating mineral fertilization cover (treatment 1) and organic fertilization cover (treatments 2 and 3, two different doses) with digestate for two years. The fresh and dry matter of fruits (g) were higher for the fertilization of organic cover with digestate than the treatment with mineral fertilization with urea. When digestate was employed as fertilizer an increase in C content was observed in soil after harvesting. Also, an excellent K and N assimilation was presented by plants and fruits analyzed. This confirms that it is possible to substitute part of the mineral fertilizer with organic fertilizer (digestate).

Keywords: Digestate · Organic fertilizer · Anaerobic digestion

1 Introduction

Agricultural sector has experimented a growing trend in energy consumption leading to higher costs and continuous deterioration of the environment. Energy consumption are referred to primary energies (motor fuels and fuels for field machinery) and to secondary energies (fertilizers employed). According IDAE [1] nitrogen mineral fertilizers account for more than half of energy costs. A clearly viable solution to this problem is to replace part of the mineral fertilizer with organic fertilizer. A sustainable agriculture is reached when the soil fertilization is improved and sometimes this is achieved adding organic matter to the soil. In Spain there are large extensions of agricultural land at risk of desertification, concretely more than two thirds of the total Spanish land [2], so organic fertilizer plays a very important role in the fight against the climate change and the desertification in the country and the world.

The anaerobic digestion is a process where organic fertilizer (called digestate) is produced through a process in the absence of oxygen in which organic matter mainly for waste is degraded by specific microorganisms to generate biogas and digestate. Digestate is a fertilizer containing odorless stabilized organic matter and NPK nutrients have changed to mineral forms that are available for plants [3]. There are some studies about digestate application to plants, some references are shown below: Mórtoła et al. [4] evaluated pots with different doses of digestate and inorganic fertilizer analyzing chemical and biological properties of soil and the growth of lettuce; Zilio et al. [5] carried out maize trials in open field for three consecutive crop seasons comparing synthetic fertilizers versus recovered fertilizers obtained from digestate; Vaish et al. [6] conducted plot experiments to explore the viability and response of three different anaerobic digestates (from three different organic waste) in the growth performance of brinjal; Coelho et al. [7] compared soil's primary plant macronutrients and microbial abundance in two species, perennial ryegrass and white clover when were applied five diverse anaerobic digestates, undigested cattle slurry, calcium ammonium nitrate and no fertilizer. All of mentioned studies achieved positive behavior in plants developments by applying anaerobic digestate with multifaceted environmental benefits.

The present study evaluates the feasibility of applying two different anaerobic digestate doses opposite to mineral fertilizer in pepper pots. Results of this study are based on a complete characterization of anaerobic digestates from anaerobic digestions process assays carried out in other research to find a high values of biogas yield. The findings of this study make it possible to know the chemical composition of soil, plant, fruit and root applying anaerobic digestate with mineral fertilizer or mineral fertilizer alone.

2 Methodology

2.1 Experimental Design

The tests carried out to study the digestate as organic fertilizer were developed with pepper plants, in pots of 0.0314 m^2 of surface and 4 repetitions per treatment. An equal fertilizer was applied for all treatments before transplant, with 50% of the necessary nitrogen for plants, and the total amount of phosphorus and potassium necessary for the pepper. The fertilizer after transplant was different for each of the 3 treatments: Control treatment (treatment 1) with nitrogen mineral fertilization applied (urea (46% N)) (50% of the necessary nitrogen was applied); Low treatment (treatment 2), the 25% of the nitrogen needs was applied with digestate; High treatment (treatment 3) applying the 50% of the nitrogen needs with digestate. The second nitrogen input was supplied to the plants in six times every 15 days. Finally, at the end of the harvest plants of each plot were divided into fruit, plants and roots. Samples of soils were taken for analysis too.

2.2 Analytical Methods

The composition of different parts of plants were carried out according United Nations Standards that appear specified subsequently. Carbon (C) and Nitrogen (N) content was determined using a True-Spec CHN Leco 4084 elementary analyzer (USA), according to

the UNE-EN 16,948 standard for biomass analysis [8]. Elements analyzed in the digestate (Ca, Fe, K, Mg, Na, P and Al) employed as fertilizer were detected by spectroscopy using an ICP-OES Varian 715 ES (Australia) using the UNE-EN 16,967 standard for biomass analysis [9]. The samples for this analysis were previously digested in a Milestone Start D microwave (Italy).

2.3 Data Analysis

A statistical treatment of results from harvest (number of fruits, stem diameter, stem length, fresh matter and dry matter plants, fresh matter and dry matter fruits) has been carried out. These results have been subjected to an ANOVA analysis (Analysis of Variance) of a factor to study the significance (p value of 0.05) in each treatment (control, low dose and high dose treatments). The statistical program used was Minitab 18.

3 Results

3.1 Digestate and Soil Composition

In the Table 1 are reflected digestates and soils composition employed to fertilize pepper plants with treatments 2 and 3 in years 1 and 2. Different digestates were employed each agricultural year as can be observed in the Table 1. For this reason are shown in Figs. 1 and 2 the soil evolution composition after to apply the digestate and mineral fertilizer for different year studied.

Table 1. Digestate composition of organic fertilizer evaluated in the two years of study.

Elemento	Soil 1	Soil 2	Digestate 1	Digestate 2
Ca, ppm	27,447 ± 249	4915 ± 84	968 ± 263	738 ± 25
Fe, ppm	22,669 ± 61	10,072 ± 27	107 ± 23	81 ± 2
K, ppm	13,117 ± 311	3955 ± 66	4951 ± 661	1739 ± 76
Mg, ppm	7367 ± 47	2426 ± 25	317 ± 117	416 ± 3
Na, ppm	3177 ± 60	854 ± 21	1830 ± 424	590 ± 19
P, ppm	3427 ± 109	694 ± 15	610 ± 83	232 ± 24
Al, ppm	32,514 ± 169	12,293 ± 132	n.d	34 ± 1
C, %	8.75 ± 0.44	9.03 ± 1.44	2.20 ± 0.48	0.90 ± 0.04
N, ppm	1630 ± 331	1549 ± 241	1093 ± 472	2022 ± 224

Digestate 1: digestate employed in the year 1 of the study.

Digestate 2: digestate employed in the year 2 of the study.

If Figs. 1 and 2 are observed, it can be seen as C content is increased in the three treatments developed in the two years after plants were harvested. This behaviour was observed by other authors [5, 6]. This increase is higher for treatments carried out with digestate in year 1 and only for treatment 3 (high dose) in year 2 (as a consequence of a

low initial C content in the digestate employed in year 2). Soil available N was slightly increased by digestate and mineral fertilizer applications at the end of the harvest. Coelho et al. [7] compared the fertilizer effects of different types of liquid anaerobic digestates on the growth of perennial ryegrass and white clover, and soil's primary plant macronutrients and the soil available N was increased by biofertilizer applications too. However K and P nutrients in all soil samples decrease clearly at the end of the harvest in year 1, mainly in the control treatment but this behaviour is not so clear in year 2. Al and Fe contents in soil throw higher values for treatment 2 and 3 than treatment 1 in the two years because digestate contribute to enrich the nutrients variability and availability against the mineral fertilizer employed in the control treatment (urea) [7–12]. In the study carried out by



Fig. 1. Digestate and soil evolution composition for three treatment evaluated in year 1.

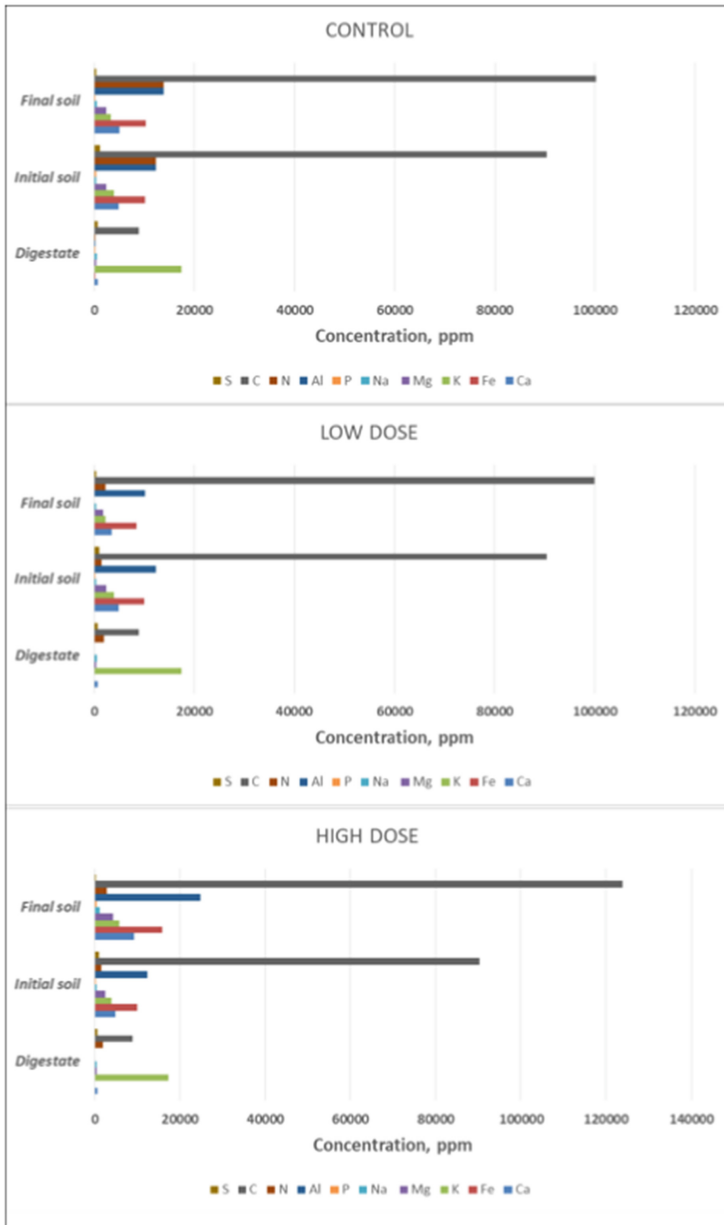


Fig. 2. Digestate and soil evolution composition for three treatment evaluated in year 2.

Wilken et al. [12] qualify the digestate as an important source of nutrients for plants and organic matter for humidification.

3.2 Effect of Digestate Application on Crop Growth

Pepper plants were harvested in 2 years (2020 and 2021). The parameters were evaluated immediately after the plants were collected are shown in the Table 2. A statistical treatment was carried out to these parameters and two of them showed significant differences: fresh matter plants and fresh matter fruit. The difference observed was not the same in the two years, for year 1 control and low dose treatments were located in different groups, however for year 2 the two group were associated to low dose and high dose treatment. Anyway fresh matter fruit is the most important parameter to evaluate the harvest production, and the results obtained show higher values for low dose treatment in two years. Also, a higher stem length can be observed for the control treatment in two years, probably the mineral fertilizer supply for the plant provide a fast growth but not increased fruit production [4, 9].

Table 2. Peppers production data in plants evaluated in pots at different doses of mineral fertilizer and organic fertilizer (digestate). Years 2020 and 2021.

	Year 1			Year 2		
	Control	Low dose	High dose	Control	Low dose	High dose
<i>Number of fruits</i>	2.50	3.25	3.00	5.25	3.50	5.25
<i>Stem diameter, cm</i>	0.93 ± 0.10	0.93 ± 0.05	1.05 ± 0.13	0.98 ± 0.10	0.90 ± 0.05	1.05 ± 0.13
<i>Stem length, cm</i>	57.00 ± 6.98	48.25 ± 6.60	50.50 ± 1.00	71.25 ± 1.50	68.50 ± 14.25	68.25 ± 7.50
<i>Fresh matter plants, g</i>	67.33 ± 17.29 a	106.78 ± 31.53 ab	113.40 ± 30.9 b	91.93 ± 9.97 ab	77.04 ± 22.71 a	105.13 ± 25.30 b
<i>Dry matter plants, %</i>	17.59 ± 1.51	16.56 ± 2.06	16.32 ± 1.00	20.27 ± 0.92	20.83 ± 1.16	20.06 ± 0.30
<i>Fresh matter fruit, g</i>	124.30 ± 39.06 a	234.70 ± 41.97 b	214.33 ± 83.59 ab	169.85 ± 39.06 a	173.68 ± 41.97 ab	236.13 ± 83.59 b
<i>Dry matter fruit, %</i>	7.95 ± 2.63	17.68 ± 7.19	15.38 ± 7.48	34.70 ± 2.63	35.21 ± 7.19	40.28 ± 7.48

Different letters in results show statistically significant differences for a confidence level of 95%.

3.3 Plants Composition Evaluation

At the end of the harvest, peppers and roots were separated from plants and each part was independently analyzed. Results obtained of this analysis were represented in Figs. 3 and 4. As it can be observed in the two Figures, K content for plants and fruits is the most elevated of all elements measured, and the difference between the three treatments is not notable. A decline in this element at the end of the harvest in soil samples was detected in Figs. 1 and 2, it means K nutrient have been absorbed mainly by plants and fruits, as expected. Other behaviour predictably have been the high value of N nutrient in fruit firstly and, plants and roots secondly. It is totally consistent with the low N content in the

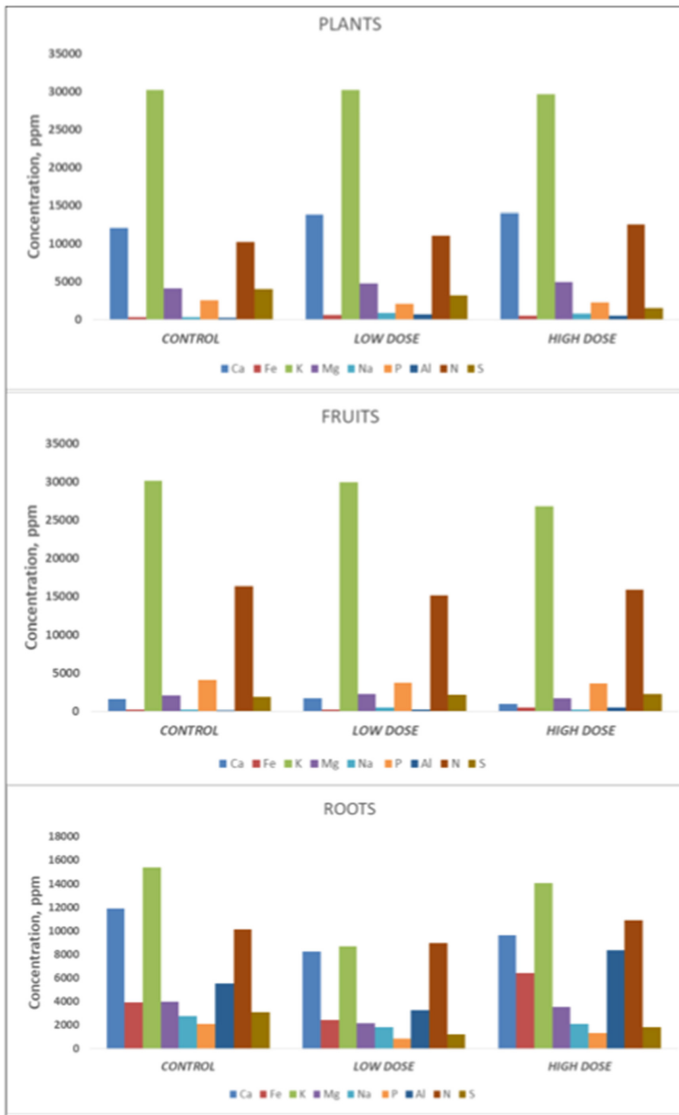


Fig. 3. Composition of plants, fruits and roots for three treatments evaluated in year 1.

soil samples shown in Figs. 1 and 2. Ehmann et al. [11] in their research about phosphates recycled from semi-liquid manure and digestate to apply as fertilizer for ornamentals, mention that a fast P uptake into plants and thus high plant availability is particularly important in the horticultural sector due to the short production periods of potted plants. It has happened in this work with pepper plants where initial concentration of P from digestate and soil (Table 1) can be represented in Figs. 3 and 4 located mainly in plants and fruits. The rest of nutrients are located in the roots of the plants. It is not found major

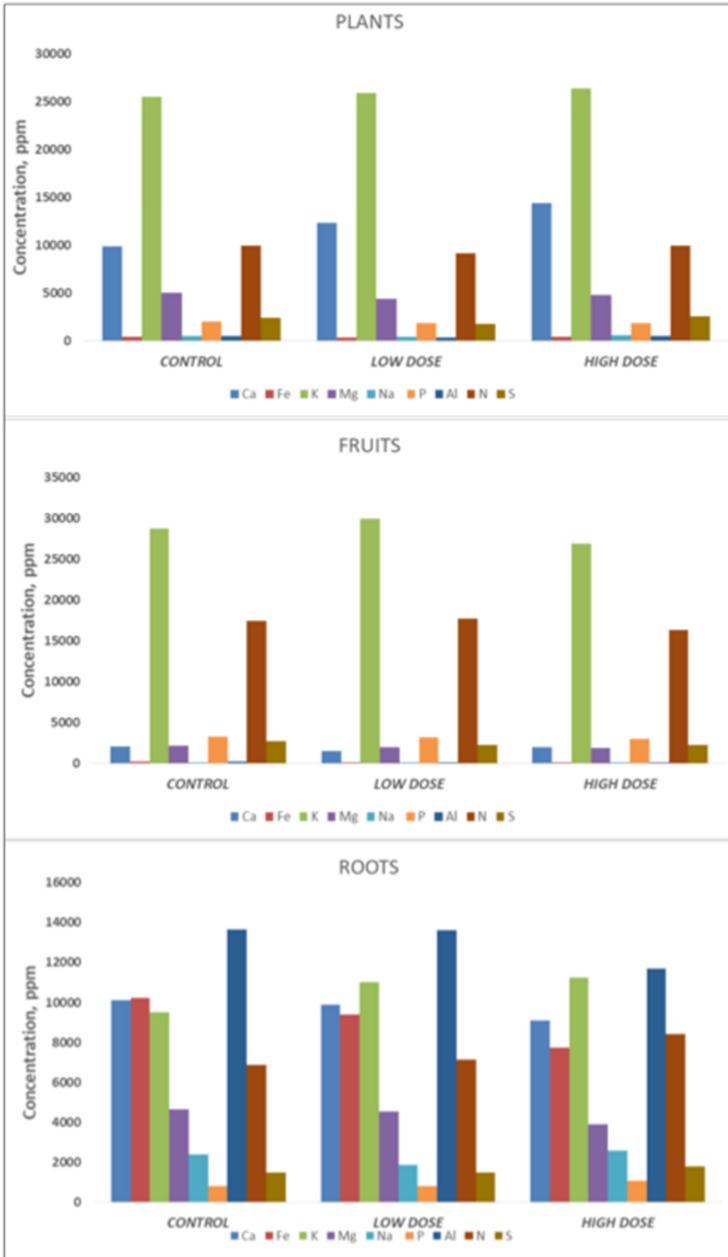


Fig. 4. Composition of plants, fruits and roots for three treatments evaluated in year 2.

differences in results obtained in year 1 and 2 for the three parts of the plants in relation to the elements contents, just to mention that Al and Fe contents from roots in year 2

were higher than year 1. This must be because of the initial composition of soil and digestate employed were different. Similar behaviour can be observed in Figs. 3 and 4 for three treatments evaluated in years 1 and 2. Zilio et al. [5] determined the elements content in maize grain produced from trials in open field comparing synthetic fertilizers versus recovered fertilizers obtained from digestate and they didn't find significant differences between the two kind of fertilizers.

4 Conclusions

The anaerobic digestates potential as fertilizers are evaluated in this work to implement this fertilizer strategy in horticulture sector in Spain due to the increase of the nitrogen mineral fertilizers. Moreover, applying this fertilizer strategy a sustainable agriculture is reaching to fight the effects of climate change. Digestate as fertilizer is an important option to replace a part of mineral fertilizer in pepper plants due to the fruit production was increased when the digestate was employed as much fertilizing after plant transplant (fresh matter fruit of 234.70 ± 41.97 g and 236.13 ± 83.59 g for low dose treatment (year 1) and high dose treatment (year 2), respectively, versus 124.30 ± 39.06 g and 169.85 ± 39.06 g for control dose treatment (years 1 and 2)). In addition, the C content increase in soil samples after harvesting was sharpest in two treatments using digestate in year 1 and in the high dose treatment in year 2. Plants and fruits composition showed elevated values of K and N nutrients at the end of the harvest and a decline in this nutrients was observed in soil samples at the same time. It means K and N nutrients were absorbed mainly by plants and fruits, as expected.

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References

1. Instituto para la Diversificación y Ahorro de la Energía (IDAE): Ahorro, Eficiencia Energética y Fertilización Nitrogenada. 1st ed. Consumos Energéticos en las Operaciones Agrícolas en España 6. España (2007)
2. Ministerio de Agricultura, Alimentación y Medio Ambiente (MAGRAMA): Impactos del cambio climático en los procesos de desertificación en España. España (2016)
3. <http://htnbiogas.blogspot.com>. Accessed 22 Mar 2022
4. Mórtoła, N., et al.: Potential use of a poultry manure digestate as a biofertiliser: evaluation of soil properties and lactuca sativa growth. *Pedosphere* **29**, 60–69 (2019)
5. Zilio, M., et al.: Using highly stabilized digestate and digestate-derived ammonium sulphate to replace synthetic fertilizers: the effects on soil, environment, and crop production. *Sci. Total Environ.* **815**, 152919 (2022)

6. Vaish, B., et al.: Explicating the fertilizer potential of anaerobic digestate: effect on soil nutrient profile and growth of *Solanum melongena* L. *Environ. Technol. Innov.* **27**, 102471 (2022)
7. Coelho, J.J., Hennessy, A., Casey, I., Woodcock, T., Kennedy, N.: Responses of ryegrass, white clover, soil plant primary macronutrients and microbial abundance to application of anaerobic digestates, cattle slurry and inorganic N-fertilizer. *Appl. Soil Ecol.* **144**, 112–122 (2019)
8. Norma UNE-EN 16948: Biocombustibles sólidos, Determinación de contenido total de C, H y N. Método instrumental (2015)
9. Norma UNE-EN 16967: Biocombustibles sólidos. Determinación de elementos mayoritarios (2015)
10. Samoraj, M., et al.: The challenges and perspectives for anaerobic digestion of animal waste and fertilizer application of the digestate. *Chemosphere* **295**, 133799 (2022)
11. Ehmann, A., Bach, I-M., Bilbao, J., Lewandowski, I., Müller, T.: Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals. *Sci. Horticul.* **243**, 440–450 (2019)
12. Wilken, D., et al.: *Digestato Como Fertilizante*. 1st edn. Fachverband Biogas e.V. Alemania (2018)



Analysis of the Mechanical Behaviour of Modified Mortars with Ash Residues from Biomass Gasification with WEEE Plastics

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Abstract. Biomass was the main source of energy for humanity until the arrival of the industrial revolution in which it was relegated to the background with the emergence of fossil fuels.

The use of residual biomass, which comes from urban solid waste (MSW) produced by humans during the development of their daily and economic activities for energy generation, is already an obligation in environments aware of energy efficiency and sustainability. The gasification of biomass is a thermochemical process for the generation of energy from it. This generation method gains a certain advantage over the rest of the alternatives thanks to the product obtained from it. Biogas, highly energetic, breaks with a usual problem that humanity has been facing for decades, since, both in gaseous and liquid form, the gas is storable and storage losses are minimal compared to other types of energy sources.

This manuscript presents a study for the recovery of residual inert by-products derived from the biomass gasification process and their use in the production of mortars to replace quarry aggregates commonly used in the production of concrete and mortar. Giving a second life to a fraction of the existing residual materials, maintaining the line of sustainability and efficiency in terms of waste management and recycling.

Keywords: Gasification · Mortars · Biomass · Sustainability · Energy efficiency · Solid urban waste

1 Introduction

This manuscript presents a comparison of mechanical uniaxial compressive strength behavior, of modified mortars versus standard mortars used usually in building. The specimens have been made in situ, therefore, in order to do a correct comparison and interpretation of the obtained results in the experimental mechanical tests one kind of

standard mortar made of Portland concrete, elaborated in the same boundary conditions, have been taken by reference. All specimens used to elaborate this paper, modified mortars and common building mortar have been manufactured using the same methodology.

According with the UNE-EN 1015-11:2020 standard Specimens have been manufactured having prismatic shape respecting standard measures, which are $160 \times 40 \times 40$ mm. The experimental requirements to elaborate this investigation are, in case of mechanical uniaxial compression test, to break tested specimens in two parts, getting six specimens with half size of standard ones. This process has done previously using the mechanical flexural strength test machine as is defined in the UNE standard.

In case of not to use hardening retarders, the European standard establish mortars specimens are tested 28 days after their manufacture immediately after put they off their conservation environment and after the necessary superficial treatments required to eliminate parts of the material that isn't correctly adhered.

In addition to 28 days experimental mechanical tests, mentioned above, this document include experimental mechanical tests of first 7 days of the mortars to evaluate the progression of their flexural and uniaxial compression strength during their hardening time.

Obtained results of mentioned mechanical tests are presented according current UNE.

2 Materials and Methods

In order to the correct experimental mechanical tests development 18 specimens, 6 made of standard Portland concrete and 12 modified specimens, have been manufactured. The modifications included in mortars 2 and 3 is a partial substitution of Portland clinker based in fly ashes recovered through a gasification process. Gasification is a thermal transformation process for which high valued energetic gas is obtained, called synthesis gas or syngas through raw material which is composed by biomass and WEEE (Waste Electrical and Electronic Equipment recycling) in this case. For the use of ashes to design modified mortars, a treatment of cleaning of inorganic elements and soluble mineral contained in ashes have done. Treatment consist in one first wash of the ashes in water and after another one in acetone [1]. Produced ashes in the gasification process are waste formed by a mixture of biomass and plastic waste which due to oxygen excess during the process do not react. Ashes are composed of tars, soluble mineral, inert, and other organic compounds. In chemical terms, the composition of ashes is SiO_2 and CaO mostly, and Mg , Al , K y P in minor [2].

To prepare necessary specimens the first step is to separate fine granulometry of the rest waste. This fine granulometry part of material is used to develop experimental tests refered in this manuscript. To start the separation of fine granulometry, compound of coal which is generated as result of gasification process was sieved. After, wash in water is done, to do this, gasification waste are put in glass receptacles and the mixture suffer an ultrasonic bath, this process delay 2 h, and later, mixture is resting for next 24 h. When this time have passed in order to eliminate water rest in the composition, mixture is filtered using Glass microfibre Discs 125 mm. The process of wash in water finish by putting the mixture in an oven during 12 h at 100 C, removing moisture of

the compound. Analogously, mixture is washed in acetone bath applying same steps to water bath. Finally, using Octagon digital CE equipment starting material was classified according to particle size through sieves of 2000 μm , 850 μm , 425 μm , 180 μm , 106 μm , 75 μm and <75 μm respectively.

At time that fine granulometry ashes have been separated of the rest of gasification waste, XRF analysis is realized verifying ashes chemical composition after the whole treatment [3]. Acetone bath presents advantages at this moment because hydrocarbon, that are present in the surface of particles, is removed preventing possible corrosion, caused by these hydrocarbons, in modified mortar specimens.

Previous heat treatments of biomass to prepare charcoal and wash operations previously above mentioned involve chemical changes in raw material. Table 1 below shows concerning values to ashes chemical composition before and after water and acetone baths.

Table 1. Chemical composition of the ashes obtained after the treatments described.

Composition	Bruto	Type2	Type2water	Type2Acetone	Type1	Type1Water	Type1Acetone
Zn	0.00	0.36	0.63	0.59	0.42	0.39	0.38
Cu	0.13	0.35	0.32	0.23	0.13	0.14	0.14
Ni	0.00	0.18	0.19	0.34	0.00	0.06	0.05
Fe	0.00	7.13	10.40	17.82	5.22	7.63	11.18
Mn	0.00	0.28	0.34	0.32	0.06	0.16	0.11
Cr	0.00	0.71	0.65	1.29	0.03	0.16	0.14
V	0.28	0.07	0.05	0.05	0.03	0.05	0.04
Ti	72.75	8.16	0.87	0.88	0.41	0.68	0.69
Sc	0.00	0.14	0.06	0.08	0.07	0.10	0.09
Ca	12.47	67.89	70.92	64.35	36.34	53.48	51.38
K	2.16	6.61	4.64	4.61	36.62	20.84	19.72
S	0.00	1.13	1.72	1.36	3.24	2.15	1.71
P	0.00	0.29	0.57	0.37	1.22	2.47	2.44
Si	0.00	4.07	6.22	5.72	8.07	8.36	8.91
Cl	11.63	2.40	2.07	1.72	7.86	3.09	2.77

After treatments suffered by ashes it shows that Ti, Ca, K and Cl quantities have been reduced. High content in chlorine and potassium can cause troubles like deposit formation, corrosion of mortars or even prevent the incorporation and use of ashes in the specimens [4]. After water and acetone baths processes, chlorine quantity was reduced in 82, 20% and 84, 80% respectively for type 2 ashes and in case of type 1 ashes level of chlorine content was reduced in 73, 43% and 76, 18%.

Fly ash, slag, metakaolin, blast furnace slag or ashes produced by rice waste are high aluminosilicated materials, acting effectively as binder in mortars and concrete manufacture [5]. Binder materials are very relevant and definitively important in mechanical

properties that final products, in this case mortars, presents after the hardening process [6].

The 90% of presented composition is based in SiO_2 , Al_2O_3 , CaO and Fe_2O_3 , and the presence of other oxides is relatively low. These oxides have the greatest influence on the compressive strength of concrete [5, 7]. Table 2 below shows chemical composition attending to oxides of resultant ashes.

Table 2. Chemical composition attending to oxides of resultant ashes.

		Type2	Type2water	Type2Acetone	Type1	Type1Water	Type1Acetone
Chemical composition of ashes	CaO	94.983	99.214	90.021	50.838	74.82	71.874
	Al_2O_3	-	-	-	-	-	-
	MgO	-	-	-	-	-	-
	SiO_2	8.698	13.309	12.228	17.259	17.883	19.056
	Na_2O	-	-	-	-	-	-
	SO_3	2.81	4.294	3.384	8.082	5.374	4.274
	P_2O_5	1.34	2.612	1.699	0	11.326	11.199
	K_2O	7.964	5.594	5.554	44.127	25.11	23.761
	TiO_2	13.605	1.449	1.461	0.677	1.136	1.148
	MnO	0.21	0.25	0.239	0.905	0.119	0.082
	Fe_2O_3	10.197	14.873	25.488	7.458	10.906	15.983

Mortar Specimens are manufactured in situ following UNE-EN- 1015-11:2020 standard. To elaborate experimental path designed in this paper 3 types of mortar are manufactured. One first group of Specimens formed by standard building mortar, hereinafter M1, composed by Portland concrete. And a Second group of modified mortar specimens based in Portland concrete too, hereinafter called M2 and M3. Modifications applied in mortars M2 and M3 are a partial substitution of Portland concrete clinker, who act as binder, by the above mentioned ashes. These ashes, who passed by different chemical and physical treatments above explained re-place, in mass, 10% of total mass of mortar binder (see Table 3).

Table 3. Composition of manufactured mortars.

Mortar Type	Composition			
	Sand [kg]	Concrete [kg]	Ashes [kg]	Water [kg]
Portland M1	4.5	1.5	0	0.9
modified M2	4.5	1.35	0.15 (Type I)	0.9
modified M3	4.5	1.35	0.15 (Type II)	0.9

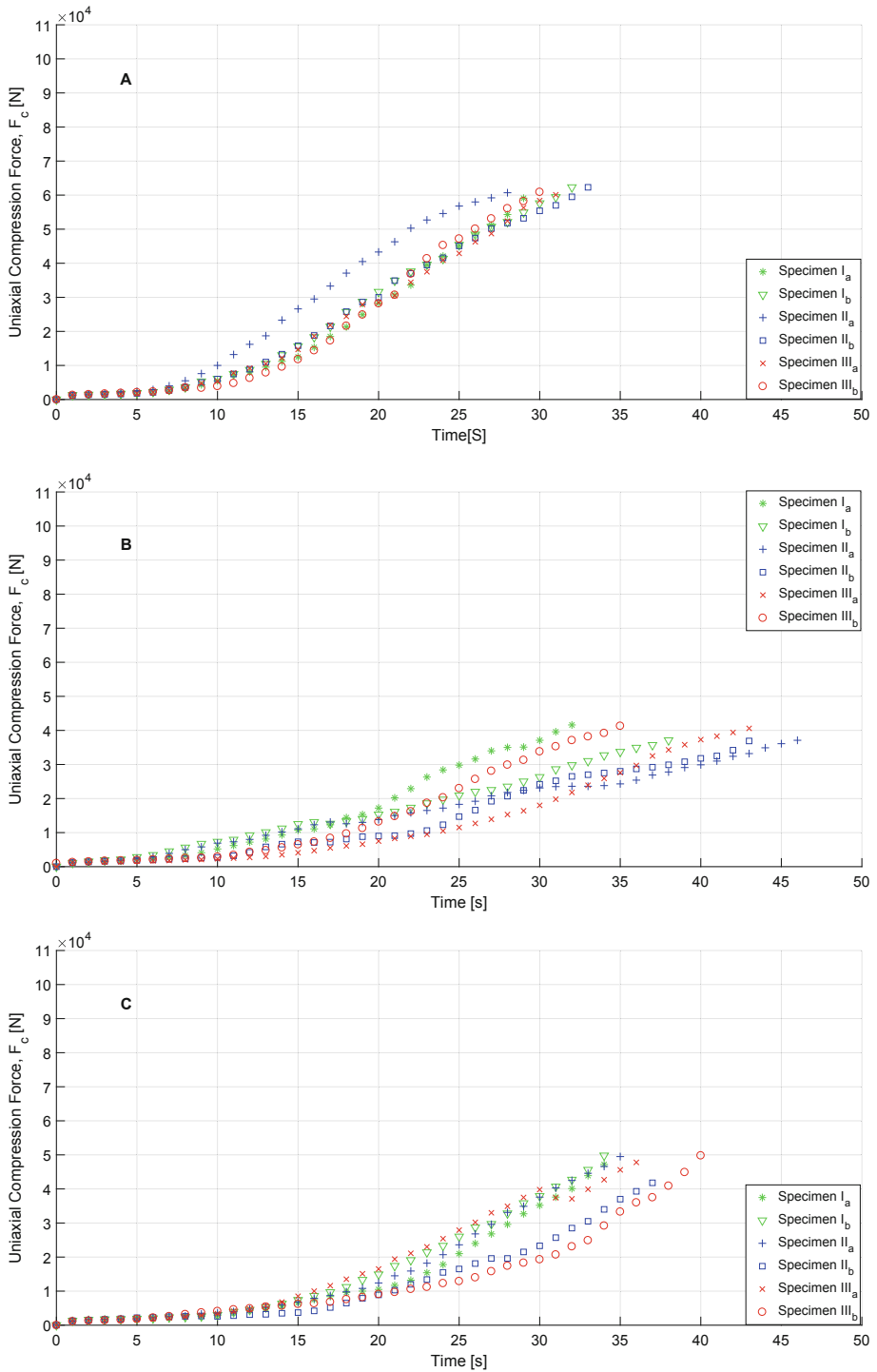


Fig. 1. Curves for specimens related to uniaxial compression force vs time in case of M1 (A), M2 (B), and M3(C) in the time of 7 days.

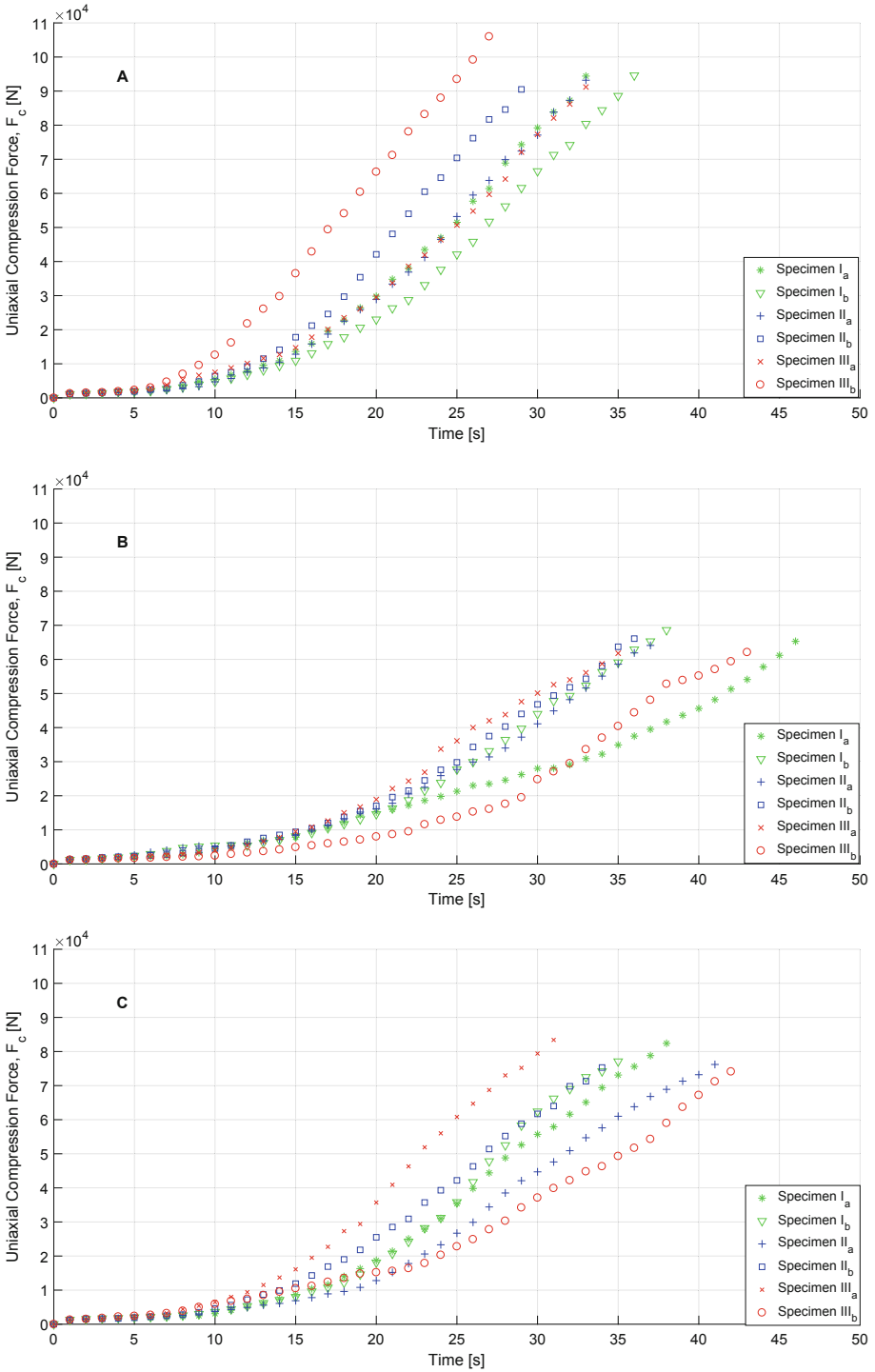


Fig. 2. Curves for specimens related to uniaxial compression force vs time in case of M1 (A), M2 (B), and M3(C) in the time of 28 days.

Following compositions described in Table 3, 18 specimens are required. Manufactured, in situ, the prismatic specimens of $160 \times 40 \times 40$ millimeters sized are grouped in 3 groups, 6 relatives to M1 mortar, 6 to M2 and 6 to M3.

3 Results

After performing the experimental mechanical test, Fig. 1a, b, c and Fig. 2a, b, c show the experimental results obtained from the uniaxial compression forces along of 7 and 28 days. These results cover the whole test, since the beginning of this one to the moment of breakage, showing the maximum load that every specimen is able to resist. From these experimental tests, uniaxial compression stresses can be determinate, according to the methodology described in the UNE-EN-101-11:2020 standard. (See Eq. 1).

$$R_c = \frac{F_c}{1,600}; \quad (1)$$

where F (N) is the load of flexural forces on the test specimens, F_c (N) represents the compressive load and 1,600 is a constant obtained by calculating the cross-sectional area of the tested specimens (mm^2) (Tables 4 and 5).

Table 4. Obtained results for uniaxial compression test for M1, M2 and M3 specimens in the time of 7 days.

Type	Specimen	Maximum Load [N]	R_c [N/mm^2]	UNE-EN-196-1:2018 Standard variation (%)	Arithmetic Mean [N/mm^2]
M1	I _a	59,100	36.95	2.94	38.1
	I _b	62,300	38.95	2.31	
	II _a	60,700	37.95	0.31	
	II _b	62,300	38.95	2.31	
	III _a	60,100	37.55	1.36	
	III _b	60,900	38.05	0.05	
M2	I _a	41,600	26.00	6.38	24.4
	I _b	37,100	23.20	5.07	
	II _a	37,100	23.20	5.07	
	II _b	36,900	23.05	5.68	
	III _a	40,600	25.40	3.92	
	III _b	41,300	25.80	5.56	
M3	I _a	47,200	29.50	1.00	30.5

(continued)

Table 4. (continued)

Type	Specimen	Maximum Load [N]	R_c [N/mm^2]	UNE-EN-196-1:2018 Standard variation (%)	Arithmetic Mean [N/mm^2]
	I _b	49,800	31.15	4.53	
	II _a	49,500	30.95	3.86	
	II _b	41,800	26.15	12.24	
	III _a	47,800	29.90	0.33	
	III _b	49,800	31.15	4.53	

Table 5. Obtained results for uniaxial compression test for M1, M2 and M3 specimens in the time of 28 days.

Type	Specimen	Maximum Load [N]	R_c [N/mm^2]	UNE-EN-196-1:2018 Standard variation (%)	Arithmetic Mean [N/mm^2]
M1	I _a	94,400	59.00	0.60	58.0
	I _b	94,600	59.15	0.37	
	II _a	93,200	58.25	1.88	
	II _b	90,500	56.55	4.74	
	III _a	91,200	57.00	3.99	
	III _b	106,000	66.25	11.58	
M2	I _a	65,300	40.80	0.94	40.4
	I _b	68,600	42.90	6.13	
	II _a	64,100	40.05	0.91	
	II _b	66,100	41.30	2.17	
	III _a	61,800	38.65	4.37	
	III _b	62,100	38.80	4.00	
M3	I _a	82,400	51.50	5.46	48.8
	I _b	77,100	48.20	1.29	
	II _a	76,500	47.80	2.11	
	II _b	75,300	47.05	3.64	
	III _a	83,400	52.15	6.78	
	III _b	74,100	46.30	5.18	

As shown in Fig. 1 a, b, c and Fig. 2a, b, c materials behaviors during compression mechanical tests are not identical. These differences are explained by the modification done in mortars compositions (See Table 3).

Figure 3 shows the progression of mechanical characteristics of the mortars during the cycle along 7 and 28 days.

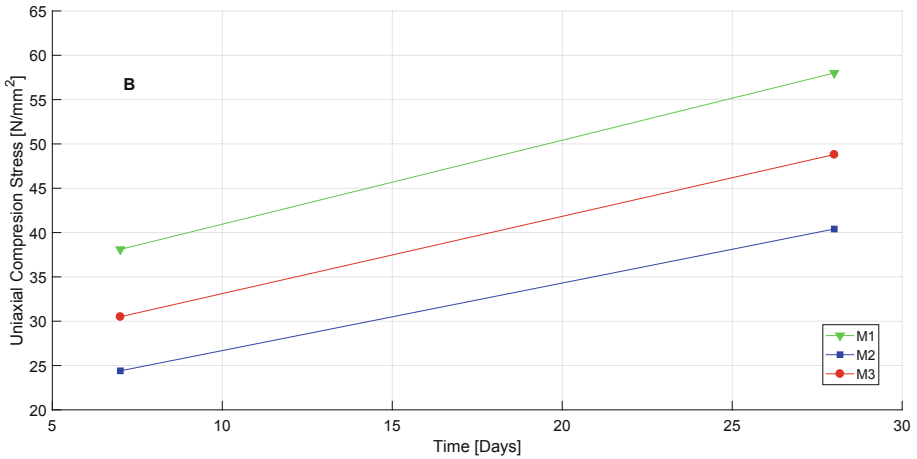


Fig. 3. Curve of axial compression strength gain of mortars along 7 and 28 days.

4 Discussions

As showing in Fig. 3 presents almost parallel curves among M1, M2 and M3, it means that progression of compression strength of mortars is similar in each case regardless of the maximum values of each. Table 6 expose that during first 7 days, uniaxial compression strength M2 result is 35.96% lower than M1 maximum value in 7 days and M3 presents losses of 19.95%, this result is 16% bigger than M2 value in this case.

Table 6. Compression strength gains by mortars first 7 days.

Type	Compression strength 7 days [N/mm ²]	Compression strength 28 days [N/mm ²]	Compression strength acquired first 7 days (%)
M1	38.1	58.0	65.69
M2	24.4	40.4	60.39
M3	30.5	48.8	62.5

In Table 7 is presented the comparison between the results obtained in the experimental mechanical tests for M2 and M3 related M1 values. In numerical way, for the

substitution of 10% of concrete clinker, mortar M3 presents loss of 15.86% of maximum compression strength in comparison with M1. On the other hand, modified mortar M2 presents loss of 30.34% in comparison with mortar M1, it means the losses are almost the double than M3, for the maximum compression strength.

Table 7. Maximum uniaxial compression strength of modified mortars M2 and M3 in comparison with M1.

Type	Uniaxial compression strength first 7 days [N/mm ²]	Uniaxial compression strength comparison first 7 days (%)	Uniaxial compression strength for 28 days [N/mm ²]	Uniaxial compression strength comparison for 28 days (%)
M1	38.1	100.00	58.0	100.00
M2	24.4	64.04	40.4	69.65
M3	30.5	80.05	48.8	84.14

5 Conclusions

As shown in the last section, discussions, the partial substitution of Portland cement clinker for recycled materials carry a diminution in the mechanical properties of new obtained mortars. In this work we have comparatively studied the mechanical uniaxial compression strength behavior, of mortars modified with ash residues from the gasification of biomass materials with plastic waste WEEE (Electrical and Electronic Equipment Waste), versus standard mortars generally used in construction.

Taking strength values of M1 as reference is shown that mortar M3 presents an intermedium behavior showing 15.63% strength losses rate, in case of M2 these losses reach 30.34% in comparison with M1. However, behavior curves (See Fig. 1a, b, c and 2a, b, c) related with mechanical uniaxial compression strength of studied mortars, which are done under the same boundary conditions to every specimen, shown M2 specimens present higher endurance in time terms in comparison with M3 specimens and this fact is even more evident in comparison with M1 specimens. It means M2 and M3 compounds, especially M2, present less fragile behavior that standard mortars. This characteristics open new favorable possibilities for some specific situations considering that fragile breakage or collapse breakage is one of the more relevant and dangerous in civil engineering.

Finally, the mechanical test results of the modified mortars must be considered in a circular economy context. It present a solution for the use and recovery of waste materials from the gasification of plastic materials. Next steps in the research is a comparison treating other variables or different behaviors of modified mortars versus other external agents for example, thermic insulation, acoustic insulation and permeability, where this kind of modifications in mortars could replace in some cases to conventional building mortars.

References

1. Libra, J.A., et al.: Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2**, 71–106 (2011). <https://doi.org/10.4155/bfs.10.81>
2. HENNE, R.A.: CARACTERIZAÇÃO DA FORMAÇÃO E DA COMPOSIÇÃO DAS CINZAS E DOS PROBLEMAS ASSOCIADOS À COMBUSTÃO DA BIOMASSA FLORESTAL EM CALDEIRA (2018)
3. Wang, W., et al.: Effect of combining water washing and carbonisation on the emissions of PM10 generated by the combustion of typical herbs. *Fuel Process. Technol.* **200**, 106311 (2020). <https://doi.org/10.1016/j.fuproc.2019.106311>
4. Jensen, P.A., Sander, B., Dam-Johansen, K.: Pretreatment of straw for power production by pyrolysis and char wash. *Biomass Bioenergy* **20**, 431–446 (2001). [https://doi.org/10.1016/S0961-9534\(01\)00005-8](https://doi.org/10.1016/S0961-9534(01)00005-8)
5. Reddy, M.S., Dinakar, P., Rao, B.H.: A review of the influence of source material's oxide composition on the compressive strength of geopolymer concrete. *Microporous Mesoporous Mater.* **234**, 12–23 (2016). <https://doi.org/10.1016/j.micromeso.2016.07.005>
6. Chi, M.: Effects of the alkaline solution/binder ratio and curing condition on the mechanical properties of alkali-activated fly ash mortars. *Sci. Eng. Compos. Mater.* **24**, 773–782 (2017). <https://doi.org/10.1515/secm-2015-0305>
7. Dunuweera, S.P., Rajapakse, R.M.G.: Cement types, composition, uses and advantages of nanocement, environmental impact on cement production, and possible solutions. *Adv. Mater. Sci. Eng.* **2018** (2018). <https://doi.org/10.1155/2018/4158682>



Seasonal Weather Sensitivity of Staple Crop Rice in South India

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Abstract. The paper examines the effect of seasonal weather variability and extremes on the mean and variance of rice yield in south India for 1990–2017. The Just and Pope stochastic production function is adopted to assess the extensive district-level data with linear and non-linear specifications. Estimation results based on feasible generalized least square method indicate that average yield and yield variability are climate-sensitive and seasonal weather variation and shock significantly influence rice production. Mean yield is observed to be primarily affected by changes in evapotranspiration and minimum temperature across seasons. Further, the minimum temperature parameter above normal is marked as a risk-increasing weather input for rice during the winter season. Countering adversities of climate change through coping strategies, region-specific policies, federal programmes and support are therefore recommended, thus pivotal for state-wide rice production and food security by extension.

Keywords: Climate impact · Rice production · Stochastic production function · South India

1 Introduction

There is widespread concern about climate variability on crop production around the world, including crops that are well adjusted to their surroundings as environmental effects on crop yield stand significant [1]. Crop yield and food security are two core issues, as innate climate change and rising demand are anticipated to impair the global economy [2]. To serve the burgeoning population, food demand is projected to grow by 60% by 2050 [3]. In 2017, approximately 10% of the world's population was threatened by food insecurity through many socio-environmental conflicts [4]. About 350 million people in India were found malnourished, with nearly 47 million children suffering from chronic malnutrition [5, 6]. Consequently, the National Food Security Act was passed by the Indian government with an aim of distributing subsidized foodgrain to roughly two-thirds of the inhabitants. This required 33.6 million metric tonnes of rice annually for

the national food distribution system [7]. Rice, one of India's dominant crops, is planted on about 43% of the farmland, with rainfed rice accounting for 52% of the overall planting area [8, 9]. Apparently, this rainfed cereal grain is often considered climate-vulnerable in southeast Asia because of limited water and land resources. Further, climate forecasts for India up until 2100 show a 2–4° climb in temperature and rise in rainfall intensity, particularly during the monsoon period [10]. Several studies have concluded that variations in seasonal precipitation and surface warming are predicted to induce dry spells and lower food availability in emerging economies, eliciting a significant risk to sustainable development. However, the climate effect on Indian agribusiness is more predominant, not only since a large chunk of the population is reliant on farming but also because there are extant pressures on resources and inadequate coping skills [11].

Numerous researchers have assessed the effect of meteorological factors on the production of rice in India. Generally, the studies have evaluated the impact using either agro-economic or econometric models. Using the fixed-effect model, Birthal et al. [12] reported that rice harvest is highly susceptible to a rise in mean temperature, whereas Patanayak and Kumar [13] documented that day and nighttime temperatures both exhibit detrimental impacts on rice output during various growing seasons. Based on panel-correlation standard error estimation, Gupta et al. [14] confirmed that paddy yield is susceptible to weather factors, while Krishnamurthy [15] showed that rice output declined up to 3% due to climate stress. Given resource availability, the effect of seasonal climate varies across regions, as does crop productivity. The southern part of India identified as a climatic hotspot is projected to witness a climb in summer and winter temperature, an upsurge in rainfall events and a rise in the number of rainy days over 2.5 mm per day. The adverse climate in southern India, comprising states such as Tamil Nadu, Andhra Pradesh, Kerala, Karnataka and Telangana, is expected to affect the primary sectors most, multiplying the socio-economic inequities [16].

Given regional disparities and alarming changes in climate parameters, many researchers have also conducted state-specific studies. According to Geethalakshmi et al. [17], rice yield is expected to fall by 41% in the Kaveri river basin, also known as Tamil Nadu's rice bowl, with temperatures reaching 4 °C. Based on panel-corrected standard error estimation, Saravanakumar [18] reported that climate factors and rice yield exhibited a quadratic relationship in Tamil Nadu from 1971 to 2009. Further, with climate change, the enormity of the decrease in rice production across various districts of Tamil Nadu from 2050–2080 is expected to be greater than the decreases from 2000–2020 and 2020–2050 [19]. Samiappan et al. [20] investigated the effect of winter monsoon on the production of rabi rice in Tamil Nadu and foreseen that with an incline in monsoon rain and heat, the crop output is predicted to rise by 10–12% in 2050 and 5–33% in 2081–2100 climate scenarios. In the erstwhile Andhra Pradesh state, Padakandla [21] assessed climate effect on the principal crops and indicated that the yield of rice alongside groundnut and tobacco crops is more affected because of climate fluctuations than is sorghum and cotton yield. Using quantile regression from 1971–2004, Barnwal and Kotani [22] reported that kharif rice is more susceptible to variations in temperature and rainfall in Andhra Pradesh, whereas the rabi rice is more resilient.

Based on field experiments, Varghese et al. [23] examined the predicted value of rice yield under future climate scenarios with constant carbon dioxide levels and varied meteorological factors in Kerala. They discovered that yield declines for planting dates and further decreases with a rising temperature affecting the crop duration. Using advanced simulation frameworks, Saseendran et al. [24] predicted temperature and rainfall during the monsoon season in Kerala are likely to rise by 1.5 °C and 2 mm per day, respectively, shortening the rice maturity period by 8%. Kumar et al. [25] found a non-significant increase in rainfall in coastal Karnataka from 1980–2013; correlation analysis revealed a frail relationship between rice harvest and rainfall, with rain accounting for around 23% of fluctuations in rice production. Using taluk-level data from Karnataka, Murari et al. [26] discovered an inverse linear association between rice yield and extreme degree days, indicating that extreme temperature results in a larger effect than rainfall and growing degree days. Using feasible generalized least squares estimation, Guntukula and Goyari [27] found that maximum temperature has a considerable negative impact on rice productivity, whereas minimum temperature is seen as a risk-increasing element for rice output in Telangana between 1956–2015. Given the climate sensitivity of the primary sector, frequent droughts and crop failures, Telangana state saw an upsurge in farmer suicide [28, 29]. Soora et al. [30] indicated weather variation is likely to favour rice production by 10–15% in Karnataka, Tamil Nadu and Andhra Pradesh, whilst Debnath et al. [31] predicted a major yield gap of above 1.5 tonnes per hectare in rice-growing southern states under future climate scenarios.

Past research on the climate effect on the production of rice in India has primarily focused on state-wise implications. Limited research has been conducted into a macro-level regional analysis considering south India as a tropical dry and wet climate zone. Implementing extensive district-level weather and non-weather data will improve accuracy in estimating the climate effect on regional rice yield. Several researches have exploited annual panel data and conventionally glanced at the effect of temperature and precipitation on aggregate yield. But there has been limited robust studies investigating the seasonal impact of other climate parameters and weather shocks on a single crop yield and on yield variability. Analysis of seasonal climate effect on the rice yield and associated variability at spatially disaggregated locations will explain the variation in rice harvest and will help in formulating policies to adapt Indian agriculture to changing climate. Thus, the present research, using stochastic frontier analysis, exploits district-level disaggregated data and assesses the effect of seasonal weather variability of five climate parameters and respective extremes on rice yield and variability, filling the research gap and contributing to existing literature.

The rest of the paper is structured as follows: the second section describes the data and methodology, the subsequent section reports the results and the last section concludes.

2 Material and Method

The study analyzes the district-level data for the five southern states of India, Tamil Nadu, Andhra Pradesh, Kerala, Karnataka and Telangana, based on the 2015 district boundary (a total of 99 districts). The district-level data was collected from the International Crops Research Institute for the Semi-Arid Tropics database for the period 1990 to 2017. The

non-weather variables included in the study are rice production, gross irrigated area, gross cropped area, total agricultural labour employed and total fertilizer consumption. The dependent variable rice yield is the proportion of rice production to rice cropped area, expressed in tonne per hectare. Given that agricultural input variables are detailed in composite form, relevant rice-particular non-weather inputs are computed through prorating [14, 21, 32].

The data on weather variables are sourced from the Terra Climate database, which holds monthly temporal high-resolution meteorological data for the global terrestrial surface for the period 1958–2019. The data is transmitted in batch operation to develop annual tables at the state level for each variable. Weather variables are considered through four Indian Meteorological Department defined seasons: Summer (March–May), Rainy (June–September) and Autumn (October–December) and Winter (January–February). The independent seasonal weather variables included are minimum and maximum temperatures, evapotranspiration, rainfall and windspeed. Labels and summary statistics of both weather and non-weather variables of interest are presented in Tables 1 and 2.

Given the possibility of a non-linear relationship between rice yield and climate, quadratic terms of seasonal weather variables are included. Further, seasonal weather anomalies are considered since seasonal weather variables deviating from climate normal are expected to affect agricultural performance. As per World Meteorological Organisation, climate normals are averages of climatology variables over at least two decades. Deviation of observed weather from such long period average (or weather anomaly) is considered normal if:

$$x_{it} \in \bar{x}_i \pm \tau \bar{x}_i \quad (1)$$

where, x_{it} is the observed weather in district i at time t , \bar{x}_i is the climate normal and τ is the climate threshold. Weather anomalies ω beyond $\pm \tau$ of \bar{x}_i capturing weather shocks takes the asymmetric response of rice yield to extreme climate events into account [32]. To compute τ , normality of variables are assumed, which is often adopted to find outliers (climate extremes). Considering 99% confidence interval, climate threshold is expressed in a percentage as:

$$\tau = \frac{Z_{0.99} \cdot \sigma}{\bar{x}_i} \times 100 \quad (2)$$

where, $Z_{0.99}$ is the z-score of 99% confidence level and σ is the standard deviation of the sample statistics. Hence, post computing τ , forty weather anomalies of five climate parameters across four seasons is constructed and written as:

$$High\omega = \begin{cases} 1 & \text{if } x_{it} \geq (1 + \tau)\bar{x}_i \\ 0 & \text{otherwise} \end{cases} \quad (3.1)$$

$$Low\omega = \begin{cases} 1 & \text{if } x_{it} \leq (1 - \tau)\bar{x}_i \\ 0 & \text{otherwise} \end{cases} \quad (3.2)$$

To quantify the effect of weather variables and extremes on yield and associated variability, controlling non-weather factors, the production frontier developed by Just and Pope [33, 34] is used as follows:

$$y = f(X, \beta) + \mu = f(X, \beta) + h(X, \theta)\varepsilon \quad (4)$$

where, y is the output, X is the vector of inputs, ε is random shock, β and θ are unknown parameters. Expected crop yield $E(y) = f(\cdot)$ and crop variability $Var(\mu) = h(\cdot)$; hence $f(\cdot)$ and $h(\cdot)$ respectively represent the mean yield and yield risk function. Based on these, regression equations estimating climate sensitivity of rice crop are written as:

$$E(y)_{it} = X_{it}\beta + Z_{it}\gamma + \alpha_i + \delta t + \epsilon_{it} \quad (5.1)$$

$$Var(\mu)_{it} = W_{it}\theta + \alpha_i + \delta t + \varepsilon_{it} \quad (5.2)$$

where, X_{it} represents the vector of seasonal weather variables in district i in time t including minimum temperature, maximum temperature, rainfall, evapotranspiration and windspeed; Z_{it} represents the vector of non-weather variables in district i in time t including agricultural labour, fertilizer used and irrigated area; W_{it} represents the vector of seasonal weather anomalies in district i in time t ; β , γ and θ are unknown parameters to be estimated; α_i are the district fixed-effects; δt is the time fixed-effects; ϵ_{it} and ε_{it} are error terms.

3 Results

Prior to estimation, weather and non-weather variables were examined for unit-root using the augmented Dickey-Fuller test and were found stationary. Since panel data is estimated utilizing either a random or fixed-effect model, the Hausman test is performed. This rejected the null hypothesis of non-correlation between district-specific effect and explanatory variables, prompting the adoption of a fixed-effect estimation. Also, the Breusch-Pagan test is used to screen for heteroscedasticity, which rejected the null hypothesis of homoscedastic variance. To account for heteroskedasticity as well as autocorrelation and cross-sectional dependence, a three-stage feasible generalized least square estimation is adopted for the Just Pope model. In the first stage, y_{it} is regressed on $f(\cdot)$ and residuals are computed. In the second stage, the natural logarithm of the square of the estimated residual is regressed on $h(\cdot)$. In the third stage, the first stage regression is reestimated applying deemed weights (predicted value of residuals) procured from the second stage. The second and third stages, respectively, provided consistent estimates of $h(\cdot)$ and $f(\cdot)$. Diagnostic tests and regression results are reported in Tables 3 and 4.

The Akaike criterion, an estimator of prediction error, showed the quality of the statistical model and the probability value of F statistics and indicated that the model is statistically significant. Durbin-Watson statistics specified the presence of trivial positive autocorrelation among residuals. The mean yield of rice is considered as a measure of weather and non-weather factors in the estimated specifications, whereas climate extremes, as reflected by weather anomalies, are considered to determine rice yield variability. The coefficient of district-fixed effect and time trend are omitted. Even so, the

latter was found positive and significant, demonstrating that technological advancement had increased mean yields and associated variability. In the second and third stages of regression, the coefficients obtained portray the marginal impacts of inputs on the mean and variance of yield. The elasticity, inflection point and semi-elasticity of non-weather, weather and anomaly inputs, respectively, are further computed to discern the range to which seasonal climate parameters influence rice production.

Increases in maximum temperature during the summer and autumn seasons decrease rice yield at an increasing rate, affecting planting and harvesting periods, with turning points at 33.15 and 33.67 °C. Likewise, during the summer and rainy season, a rise in minimum temperature reduces yield at an increasing rate, obstructing the planting and growing period, with shifting points at 27.20 and 26.93 °C, respectively. But as the minimum temperature increases beyond 22.78° in the autumn season, the expected yield declines as the harvesting is affected. Warmer climate protects plants from pest attacks, but temperature above optimal level with increased moisture loss is harmful for rice production, damaging root growth.

Turning now to essential water elements for a crop cycle, an increase in rainfall during the rainy seasons decreases yield at an increasing rate, affecting the growing period, with a turning point of 812.03 mm. But during winter seasons, heavy rain rises rice yield at a rising rate with a shifting point of -46.80 mm. Though rice flourishes in flooded soil, intense rain causes oxygen deficiency that damages temperate crops during the growing period. As evapotranspiration, quantifying the water use in the rice production process, increases beyond 105.05 and 30.92 mm in summer and winter, the expected yield drops as the planting period is mainly impeded. Similarly, a rise in evapotranspiration during the rainy season reduces rice yield at an increasing rate, affecting the growing period, with a turning point at 83.77 mm. Higher evapotranspiration coupled with solar radiation dries out the soil, physically impairs plants and affects germination. Moving on to consider the velocity of wind, as windspeed rises above 1.52 m per second in the winter season, yields decline. Moderate wind favours plants by increasing carbon dioxide supply, but strong wind knocks plants over, abrading the plant tissues.

Variability in rice yield is mainly found to be sensitive to the minimum nighttime temperature. A minimum temperature of 1 °C below climate normal in the winter season increases yield variability by 251.01%. Likewise, as the minimum temperature in the winter season exceeds the climate normal by a unit, yield variability increases by 317.67%. Because of the higher minimum temperatures, increased seasonal heat-flux during nighttime poses a greater effect on rice yield risk than on vegetative growth, because of the increased rate of senescence. Considering the non-weather factors, with a yield elasticity of 0.04, rice production increased by 848.0 kilos per hectare when an added tonne of fertilizer was practiced per unit of gross cultivated area. Similarly, a unit increase in the irrigated area raises mean yield by 1300.8 kilos per hectare with a yield elasticity of 0.18. Given rice farming is input-intensive, adequate nitrogen fertilizer use and irrigation expansion provide the required nutrients, allowing for a consistent food supply.

4 Conclusion

Using the Just and Pope production function, this paper examined the impact of non-climate and climate factors on rice yield and variability in south India from 1990 to 2017. This study relied on district-level panel data, reflecting a larger magnitude of estimated changes in rice production to relative changes in the weather pattern, undertaking seasonal measures of the following climate parameters: minimum and maximum temperatures, rainfall, evapotranspiration and windspeed. It furthermore expands the research by incorporating seasonal weather anomalies to assess weather shocks, allowing for asymmetric climate effects by separately estimating positive and negative anomalies. Since non-weather variables could either increase or decrease production risk, the analysis controls these factors when evaluating the production frontier. The estimation results indicate that average yield and yield variability are climate-sensitive and seasonal weather variations and extremes significantly influence rice production.

Rice yield is found to be sensitive to changes in evapotranspiration, maximum and minimum temperature in the summer season, while in the rainy season, shifts in minimum temperature rainfall and evapotranspiration are observed to affect yield. In the autumn season, variation in rainfall, windspeed and evapotranspiration are found to influence mean yield, while rice yield is reported susceptible to changes in minimum and maximum temperature in the winter season. Analysis showed that expected yield across seasons is primarily influenced by two climate parameters: evapotranspiration and minimum temperature. Furthermore, the minimum temperature above normal is observed as a risk-increasing weather input for rice during the winter season. As it happens, all non-weather inputs are reported positively related to rice yield, as Pattanayak and Kumar [13] found. Also, present empirical outcomes converge towards that of Arshad et al. [35], Arumugam et al. [36] and Poudel et al. [37]. As Barnwal and Kotani [22] noted, increased temperature is found to decrease the yield and increased rain is found to increase the yield. Seasonal differences in surface temperature and precipitation influence crop yields through their effect on plant development, whereas weather anomalies sway farmer crop management decisions.

The current study underscores the importance of implementing appropriate policy measures, making south Indian agriculture more resilient to changing climate. Given the dominance of the primary sector and economic relevance of this principal staple crop to south India as well as the national economy, weather fluctuations are expected to exacerbate the annual rice availability with elevated price volatility [38], worsening the production and the state of the poor. Changes in cropping patterns, the installation of climate-smart systems, changes in land use, crop diversification, the selection of short-duration varieties, the introduction of high-yielding temperature-tolerant varieties using genetic approaches, insurance provision and improved irrigation are examples of coping mechanisms that ought to be implemented [39, 40]. Delaying profound adaptation efforts by even ten years might double the adaptation cost [16]. Countering adversities of changing climate through mitigation and adaptation strategies, region-specific policies, federal programmes and support are therefore recommended, thus pivotal for state-wide rice production and, by extension, food security.

Appendix

Table 1. (Variable labels)

Variable	Label	Variable	Label
Yield	Yield in tonne per hectare	WSR2	Square of windspeed in rainy season
AgriLab	Number of agricultural labour per hectare	WSA2	Square of windspeed in autumn season
FertCons	Fertilizer consumption in tonne per hectare	MXT1	High maximum temperature anomaly in winter season
IrriArea	Irrigation area per hectare	MXT2	Low maximum temperature anomaly in winter season
MAXTW	Maximum temperature in winter season	MXT3	High maximum temperature anomaly in summer season
MAXTS	Maximum temperature in summer season	MXT4	Low maximum temperature anomaly in summer season
MAXTR	Maximum temperature in rainy season	MXT5	High maximum temperature anomaly in rainy season
MAXTA	Maximum temperature in autumn season	MXT6	Low maximum temperature anomaly in rainy season
MAXTW2	Square of maximum temperature in winter season	MXT7	High maximum temperature anomaly in autumn season
MAXTS2	Square of maximum temperature in summer season	MXT8	Low maximum temperature anomaly in autumn season
MAXTR2	Square of maximum temperature in rainy season	MNT1	High minimum temperature anomaly in winter season
MAXTA2	Square of maximum temperature in autumn season	MNT2	Low minimum temperature anomaly in winter season
MINTW	Minimum temperature in winter season	MNT3	High minimum temperature anomaly in summer season
MINTS	Minimum temperature in summer season	MNT4	Low minimum temperature anomaly in summer season
MINTR	Minimum temperature in rainy season	MNT5	High minimum temperature anomaly in rainy season
MINTA	Minimum temperature in autumn season	MNT6	Low minimum temperature anomaly in rainy season

(continued)

Table 1. (continued)

Variable	Label	Variable	Label
MINTW2	Square of minimum temperature in winter season	MNT7	High minimum temperature anomaly in autumn season
MINTS2	Square of minimum temperature in summer season	MNT8	Low minimum temperature anomaly in autumn season
MINTR2	Square of minimum temperature in rainy season	RA1	High rainfall anomaly in winter season
MINTA2	Square of minimum temperature in autumn season	RA2	Low rainfall anomaly in winter season
RFW	Rainfall in winter season	RA3	High rainfall anomaly in summer season
RFS	Rainfall in summer season	RA4	Low rainfall anomaly in summer season
RFR	Rainfall in rainy season	RA5	High rainfall anomaly in rainy season
RFA	Rainfall in autumn season	RA6	Low rainfall anomaly in rainy season
RFW2	Square of rainfall in winter season	RA7	High rainfall anomaly in autumn season
RFS2	Square of rainfall in summer season	RA8	Low rainfall anomaly in autumn season
RFR2	Square of rainfall in rainy season	EV1	High evapotranspiration anomaly in winter season
RFA2	Square of rainfall in autumn season	EV2	Low evapotranspiration anomaly in winter season
EVW	Evapotranspiration in winter season	EV3	High evapotranspiration anomaly in summer season
EVS	Evapotranspiration in summer season	EV4	Low evapotranspiration anomaly in summer season
EVR	Evapotranspiration in rainy season	EV5	High evapotranspiration anomaly in rainy season
EVA	Evapotranspiration in autumn season	EV6	Low evapotranspiration anomaly in rainy season
EVW2	Square of evapotranspiration in winter season	EV7	High evapotranspiration anomaly in autumn season
EVS2	Square of evapotranspiration in summer season	EV8	Low evapotranspiration anomaly in autumn season

(continued)

Table 1. (continued)

Variable	Label	Variable	Label
EVR2	Square of evapotranspiration in rainy season	WS1	High windspeed anomaly in winter season
EVA2	Square of evapotranspiration in autumn season	WS2	Low windspeed anomaly in winter season
WSW	Windspeed in winter season	WS3	High windspeed anomaly in summer season
WSS	Windspeed in summer season	WS4	Low windspeed anomaly in summer season
WSR	Windspeed in rainy season	WS5	High windspeed anomaly in rainy season
WSA	Windspeed in autumn season	WS6	Low windspeed anomaly in rainy season
WSW2	Square of windspeed in winter season	WS7	High windspeed anomaly in autumn season
WSS2	Square of windspeed in summer season	WS8	Low windspeed anomaly in autumn season

Table 2. (Descriptive statistics and stationarity check)

	Descriptive statistics			Augmented Dickey-Fuller test							
	Mean	Variance		Mean	Variance		chi2	Prob > chi2		chi2	Prob > chi2
Yield	2.7307	0.9502	RFW	9.5154	197.2757	Yield	684.1295	0.0000	RFW	2838.1215	0.0000
FertCons	0.1449	0.0102	RFS	51.6969	1711.9632	FertCons	427.6974	0.0000	RFS	2699.1603	0.0000
AgriLab	1.0066	0.3741	RFR	212.6664	51,554.8649	AgriLab	336.8273	0.0000	RFR	2038.3811	0.0000
IrriArea	0.3827	0.0498	RFA	117.6774	5268.4851	IrriArea	415.9711	0.0000	RFA	1832.2948	0.0000
MAXTW	30.9221	1.9838	EVW	38.5843	832.7628	MAXTW	2121.9727	0.0000	EVW	2087.3839	0.0000
MAXTS	35.0469	5.8863	EVS	56.4092	870.2671	MAXTS	2950.5180	0.0000	EVS	2798.3686	0.0000
MAXTR	31.1270	10.0142	EVR	92.9336	664.5672	MAXTR	1501.6028	0.0000	EVR	1664.9216	0.0000
MAXTA	29.4219	2.1994	EVA	85.0084	505.6674	MAXTA	802.7165	0.0000	EVA	1908.6518	0.0000
MINTW	19.1186	4.6758	WSW	1.7453	0.2217	MINTW	1263.0186	0.0000	WSW	597.3533	0.0000
MINTS	23.4742	4.1764	WSS	2.0244	0.1332	MINTS	1707.2087	0.0000	WSS	543.4573	0.0000
MINTR	23.0011	5.9739	WSR	2.5976	0.2876	MINTR	1123.7963	0.0000	WSR	365.1888	0.0000
MINTA	20.1486	4.9038	WSA	1.5720	0.1912	MINTA	1210.0548	0.0000	WSA	356.2514	0.0000

Numerically formatted to four decimal places.

Table 3. (Diagnostics tests)

Pre estimation			Post estimation		
				Mean equation	Variance equation
	chi2	Prob > chi2	F-stats	577.4731	3.6333
Hausman	262.0670	0.0000	P-value(F)	0.0000	0.0000
Breusch-Pagan	3099.7300	0.0000	Log-likelihood	-5237.3660	-4628.5410
			Akaike criterion	10,564.7300	9529.0830
			Schwarz criterion	10,818.5200	10,296.0700
			Hannan-Quinn	10,657.7300	9810.1540
			Rho		0.0108
			Durbin-Watson		1.9076

Numerically formatted to four decimal places.

Table 4. (Panel regression estimation)

	Mean equation			Variance equation			Std. error	Coefficient	Std. error			
	Coefficient	Std. error		Coefficient	Std. error							
Const	35.6986	***		0.0008	0.0014	const	-7.1506	**	3.6324	RA6	0.2278	0.8409
AgriLab	0.0471			0.0000	0.0000	MXT1	-0.2061		0.9840	RA7	0.1060	0.5182
FertCons	0.8480	***		-0.0016	0.0002	MXT2	-0.9975		0.9843	RA8	0.1580	0.5660
IrriArea	1.3008	***		0.0000	0.0000	MXT3	0.0716		0.3087	EV1	-0.2939	0.7269
MAXTW	-0.3333			0.0005	0.0009	MXT4	0.3336		0.3116	EV2	-0.3926	0.7290
MAXTW2	0.0090	**		0.0000	0.0000	MXT5	-0.5646		0.4820	EV3	0.3328	0.4692
MAXTS	-0.4574	**		0.0159	0.0027	MXT6	-0.5224		0.4673	EV4	-0.0104	0.4751
MAXTS2	0.0069	**		-0.0003	0.0000	MXT7	-0.2656		0.3947	EV5	0.1317	0.4724
MAXTR	0.0211			0.0048	0.0026	MXT8	-0.1636		0.4079	EV6	0.3044	0.4617
MAXTR2	0.0009			0.0000	0.0000	MNT1	3.1767	**	1.4177	EV7	-0.9065	0.6487
MAXTA	-1.2548	***		-0.0075	0.0039	MNT2	2.5101	**	1.2046	EV8	-1.0072	0.6744
MAXTA2	0.0186	***		0.0000	0.0000	MNT3	0.1118		0.4156	WS1	0.7532	0.5067

(continued)

Table 4. (continued)

	Mean equation				Variance equation						
	Coefficient	Std. error		Std. error	Coefficient	Std. error		Std. error			
MINTW	0.1289	0.1742	EVA	0.0047	0.0050	MNT4	0.5490	0.4361	WS2	0.7500	0.5174
MINTW2	-0.0008	0.0045	EVA2	0.0000	0.0000	MNT5	0.2789	0.7139	WS3	0.4750	0.4081
MINTS	-1.0132	0.2703	WSW	0.6654	**	MNT6	0.5097	0.6945	WS4	0.2764	0.4138
MINTS2	0.0186	0.0057	WSW2	-0.2196	***	MNT7	0.1073	2.3668	WS5	0.0775	0.5651
MINTR	-0.4778	0.2297	WSS	-0.1681		MNT8	0.0000	0.0000	WS6	-0.0465	0.6035
MINTR2	0.0089	0.0049	WSS2	0.0770		RA1	-0.2109	0.3979	WS7	0.0089	0.9587
MINTA	1.0213	0.1981	WSR	-0.0501		RA2	-0.1901	0.4018	WS8	0.3497	0.9888
MINTA2	-0.0224	0.0050	WSR2	0.0398		RA3	-0.0290	0.2860			
RFW	0.0086	0.0026	WSA	-0.0689		RA4	0.0805	0.2822			
RFW2	0.0001	0.0000	WSA2	0.0304		RA5	-0.0321	0.8648			

Numerically formatted to four decimal places.

* $p < 0.1$, ** $p < 0.05$, *** $p < 0.01$.

References

1. Fofana, I.: Simulating the impact of climate change and adaptation strategies on farm productivity and income, a bio-economic analysis. IFPRI (2011)
2. Bodirsky, B.L., Rolinski, S., Biewald, A., Weindl, I., Popp, A., Lotze-Campen, H.: Global food demand scenarios for the 21st century. *PLoS One* **10** (2015). <https://doi.org/10.1371/journal.pone.0139201>
3. Alexandratos, N., Bruinsma, J.: World agriculture towards 2030/2050: the 2012 revision. FAO (2012). <https://doi.org/10.22004/ag.econ.288998>
4. Ten Berge, H.F.M., et al.: Maize crop nutrient input requirements for food security in sub-Saharan Africa. *Global Food Secur.* **23**, 9–21 (2019). <https://doi.org/10.1016/j.gfs.2019.02.001>
5. Sridhar, D.: Hungry for change: the World Bank in India. *South Asia Res.* **28**, 147–168 (2008). <https://doi.org/10.1177/026272800802800202>
6. United Nations: India: Nutrition and food security. <https://in.one.un.org/un-priority-areas-in-india/nutrition-and-food-security/>. Accessed 09 Mar 2022
7. Debnath, D., Babu, S., Ghosh, P., Helmar, M.: The impact of India's food security policy on domestic and international rice market. *J. Policy Model.* **40**, 265–283 (2018). <https://doi.org/10.1016/j.jpolmod.2017.08.006>
8. Bhambure, A.B., Kerkar, S.: Traditionally cultivated rice varieties in coastal saline soils of India (2016)
9. Das, K., Baruah, K.K.: A comparison of growth and photosynthetic characteristics of two improved rice cultivars on methane emission from rainfed agroecosystem of northeast India. *Agric. Ecosyst. Environ.* **124**, 105–113 (2008). <https://doi.org/10.1016/j.agee.2007.09.007>
10. Kumar, K.S.K.: Climate sensitivity of Indian agriculture. Madras School of Economics, Chennai (2009)
11. Mendelsohn, R., Dinar, A., Williams, L.: The distributional impact of climate change on rich and poor countries. *Environ. Dev. Econ.* **11**, 159–178 (2006). <https://doi.org/10.1017/S1355770X05002755>
12. BIRTHAL, P., Khan, M.T., Negi, D., Agarwal, S.: Impact of climate change on yields of major food crops in India: implications for food security. *Agricultural Economics Research Review.* **27**, (2014).
13. Pattanayak, A., Kumar, K.S.K.: Weather sensitivity of rice yield: evidence from India. *Clim. Change Econ.* **05**, 1450011 (2014). <https://doi.org/10.1142/S2010007814500110>
14. Gupta, S., Sen, P., Srinivasan, S.: Impact of climate change on the Indian economy: evidence from food grain yields. *Clim. Change Econ.* **05**, 1450001 (2014). <https://doi.org/10.1142/S2010007814500018>
15. Krishnamurthy, C.K.B.: The distributional impacts of climate change on Indian agriculture: a quantile regression approach. Madras School of Economics, Chennai (2012)
16. Vidhya, S., Murthy, I.K.: District-level changes in climate: historical climate and climate change projections for the southern states of India. CSTEP (2022)
17. Geethalakshmi, V., et al.: Climate change impact assessment and adaptation strategies to sustain rice production in Cauvery basin of Tamil Nadu. *Curr. Sci.* **101**, 342–347 (2011)
18. Saravanakumar, V.: Impact of climate change on yield of major food crops in Tamil Nadu. SANDEE, India (2015)
19. Srivani, O., Geethalakshmi, V., Jagannathan, R., Bhuvanewari, K., Guruswamy, L.: Impact of future climate change on growth and productivity of rice crop in Tamil Nadu. *Asian J. Agric. Res.* **1**, 119–124 (2007). <https://doi.org/10.3923/AJAR.2007.119.124>
20. Samiappan, S., Hariharasubramanian, A., Venkataraman, P., Jan, H., Narasimhan, B.: Impact of regional climate model projected changes on rice yield over southern India. *Int. J. Climatol.* **38**, 2838–2851 (2018). <https://doi.org/10.1002/joc.5466>

21. Padakandla, S.R.: Climate sensitivity of crop yields in the former state of Andhra Pradesh. India. *Ecol. Ind.* **70**, 431–438 (2016). <https://doi.org/10.1016/j.ecolind.2016.06.008>
22. Barnwal, P., Kotani, K.: Impact of variation in climatic factors on crop yield: a case of rice crop in Andhra Pradesh, India. IUG Research Institute, International University of Japan (2010)
23. Varghese, S.J., Surendran, S., Ajithkumar, B., Rajendran, K., Kitoh, A.: Future changes in rice yield over Kerala using climate change scenario from high resolution global climate model projection. *J. Earth Syst. Sci.* **129**, 192 (2020). <https://doi.org/10.1007/s12040-020-01459-0>
24. Saseendran, S.A., Singh, K.K., Rathore, L.S., Singh, S.V., Sinha, S.K.: Effects of climate change on rice production in the tropical humid climate of Kerala. *India Clim. Change* **44**, 495–514 (2000). <https://doi.org/10.1023/A:1005542414134>
25. Kumar, H.M.V., Shivamurthy, M., Lunagaria, M.M.: Impact of rainfall variability and trend on rice yield in coastal Karnataka. *J. Agrometeorol.* **19**, 286–287 (2017)
26. Murari, K.K., Mahato, S., Jayaraman, T., Swaminathan, M.: Extreme temperatures and crop yields in Karnataka. *India J.* **8**, 92–114 (2018)
27. Guntukula, R., Goyari, P.: Climate change effects on the crop yield and its variability in Telangana. *India Stud. Microecon.* **8**, 119–148 (2020). <https://doi.org/10.1177/2321022220923197>
28. Parida, Y., Dash, D.P., Bhardwaj, P., Chowdhury, J.R.: Effects of drought and flood on farmer suicides in Indian states: an empirical analysis. *Econ. Disasters Climate Change* **2**, 159–180 (2018). <https://doi.org/10.1007/s41885-018-0023-8>
29. Tada, D.P.R.: Distress and the deceased; farmers suicides in Andhra Pradesh; a plausible solution. *IUP J. Appl. Econ.* **3**, 47–59 (2004)
30. Soora, N.K., Aggarwal, P.K., Saxena, R., Rani, S., Jain, S., Chauhan, N.: An assessment of regional vulnerability of rice to climate change in India. *Clim. Change* **118**, 683–699 (2013). <https://doi.org/10.1007/s10584-013-0698-3>
31. Debnath, S., Mishra, A., Mailapalli, D.R., Raghuwanshi, N.S., Sridhar, V.: Assessment of rice yield gap under a changing climate in India. *J. Water Clim. Change* **12**, 1245–1267 (2020). <https://doi.org/10.2166/wcc.2020.086>
32. Verma, S., Gupta, S., Sen, P.: Does climate change make foodgrain yields more unpredictable? evidence from India. CESifo (2020)
33. Just, R.E., Pope, R.D.: Stochastic specification of production functions and economic implications. *J. Economet.* **7**, 67–86 (1978). [https://doi.org/10.1016/0304-4076\(78\)90006-4](https://doi.org/10.1016/0304-4076(78)90006-4)
34. Just, R.E., Pope, R.D.: Production function estimation and related risk considerations. *Am. J. Agric. Econ.* **61**, 276–284 (1979). <https://doi.org/10.2307/1239732>
35. Arshad, M., Amjath-Babu, T.S., Krupnik, T.J., Aravindakshan, S., Abbas, A., Kächele, H., Müller, K.: Climate variability and yield risk in South Asia's rice–wheat systems: emerging evidence from Pakistan. *Paddy Water Environ.* **15**, 249–261 (2017). <https://doi.org/10.1007/s10333-016-0544-0>
36. Arumugam, S., KR, A., Kulshreshtha, S.N., Vellangany, I., Govindasamy, R.: Yield variability in rainfed crops as influenced by climate variables: a micro level investigation into agro-climatic zones of Tamil Nadu, India. *Int. J. Clim. Change Strat. Manag.* **7**, 442–459 (2015). <https://doi.org/10.1108/IJCCSM-08-2013-0096>
37. Poudel, M., Chen, S.-E., Huang, W.-C.: Climate influence on rice, maize and wheat yields and yield variability in Nepal. *J. Agric. Sci. Technol. B.* **4**, 38–48 (2014)

38. Piesse, J., Thirtle, C.: Three bubbles and a panic: an explanatory review of recent food commodity price events. *Food Policy* **34**, 119–129 (2009). <https://doi.org/10.1016/j.foodpol.2009.01.001>
39. Jasna, V.K., Som, S., Roy Burman, R., Padaria, R., Sharma, J.: Socio economic impact of climate resilient technologies. *Int. J. Agric. Food Sci. Technol.* **5**, 185–190 (2014)
40. Sanglestsawai, S., Rodriguez, D.G.P., Rejesus, R.M., Yorobe, J.M.: Production risk, farmer welfare, and Bt corn in the Philippines. *Agric. Res. Econ. Rev.* **46**, 507–528 (2017). <https://doi.org/10.1017/age.2017.1>



Energetic Sustainable Transition Process Optimization in Terms of LCA Using CLEWs Tools

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Abstract. Ensuring a sustainable transition process, whether at a global or local level, involves designing an energy mix appropriate to the user's needs. The aim is to identify the optimal future strategy that maximizes both socio-economic benefits and sustainability. To address these challenges, multiple modeling tools are now available to assess different scenarios before implementation. However, modeling tools are generally designed for economic optimization. This is the case with the Open-Source Energy Modeling System (OSeMOSYS) a CLEWs tool. This paper proposes an optimization methodology in terms of sustainability, introducing Life Cycle Assessment (LCA) as a global estimator. In particular, the effects of energy payback times (EPBT) on the selection of transition scenarios will be evaluated. To ensure the reproducibility of the study, we present an exercise that uses data for a fictitious country that shares features of both a developing and a developed country (Atlantis).

Keywords: Sustainable energetic transition · CLEWs · OSeMOSYS · Life cycle analysis · Energy payback time

1 Introduction

Climate resilience requires optimal management of vital resources: Energy, Water, and Food or land use (EWF). The management of these resources relies on several factors like technology and fuel choices, resource availability, and market factors, which can all be affected by national resource policies [1]. These resources are strongly interlinked and comprise a coherent system (also called “Nexus”). For example, energy from fossil fuels has a direct effect on GHG emissions and then extreme droughts caused by climate changes can lead to significant food and energy security problems due to intensified water supply stress [2].

Nowadays, several models for optimizing resource management are widely used [3]. In particular, one of the most accepted namely Climate, Land, Energy, and Water systems (CLEWs), arose to clarify the connections between different actions and their possible

consequences [4] both in the medium and long term. Indeed, CLEWs is an open-source linear predictive model, sequentially EWF resolved.

Energy transition toward Renewable Energy (RE) as recommended by the Sustainable Development Goals (SDG 7), raises questions about economical and reliability issues. Nevertheless, some RE technical solutions are not economically competitive within the long-term time frame. However, for an adequate energy planning system, economic optimization is not enough. Other optimization criteria linked to sustainability need to be added.

Modeling an energy system and its relevant scenarios is complex, likewise flexible and open tools will be increasingly useful to test out new hypotheses and approaches [5, 6]. Indeed, the Open Source Modeling System (OSeMOSYS) a CLEWs tool, a newly developed open-source systems optimization model covering a medium- to long-term time frame [7], is well suited for this purpose. OSeMOSYS can be freely applied following the user's needs, thus in the present case, through its interface known as Model Management Infrastructure (MoManI), a set of scenarios are modeled. Employing OSeMOSYS and MoManI, users can create and add individual blocks into a common model, model step creation is fully described in [8].

The review of the literature revealed that authors including [9–12], developed within the OSeMOSYS core for economical optimization, methodologies relying on constraints including costs evaluations, CO₂ emissions activity, energy efficiency, energy security, etc. None of these constraints address the sustainability context. Therefore, this paper aims to develop a methodology aiming to model and provide an optimal evaluation of sustainable transition scenarios across an adequate mix of energy generations technologies not by considering a single criterion (technical or economical) but from a sustainability perspective as a multicriteria approach by introducing the Life Cycle Assessment (LCA) concept, as a sustainability estimator [13, 14]. For that, the LCA indicators will be involved in OSeMOSYS as an optimization procedure. The algebraic formulation of the modified and remaining code and the code itself [15], are provided as an online supplement to this paper. For this early stage of work, the corresponding energetic sustainability indicator, the Energy Payback Time (EPBT) has been included and evaluated.

To simplify the identification of the optimization effects in terms of the energetic sustainability, a well-known nexus framework, named Atlantis is considered [8]. Even if Atlantis nexus defaults data and its build methodology might not be realistic but is interesting because of the implication of several technologies used in its modeling including renewable and non-renewable energies. A set of scenarios are defined, and the obtained results are compared considering the optimization estimators both only economic factors and including additional energetic sustainability constraints.

The current analysis relies on a fictive country data example but allowed us to confirm the possibility to conduct a sustainability evaluation into OSeMOSYS energy mix planning for an economical optimization. So, Scenarios comparison will allow pointing out the importance of considering EPBT estimator actions alongside the objective of integrating RE in a target nexus.

2 Methodology

In this paper, the Atlantis nexus example of OSeMOSYS has been used to evaluate how the application of the energetic sustainability indicator affects the energetic mixing optimization. Atlantis is a fictional country that shares features of both a developing and a developed country. This energy model is developed by [16] as an exercise demonstrating the use of MoMani. The data (Technical and economical) used in Atlantis are not specific for any country but were extracted from the International Renewable Energy Agency reports and IEA-Energy Systems Analysis Program -Technology briefs (E01, E02, E03, E06, E10, and E11).

Different scenarios linked to nuclear and Solar technology are evaluated using strictly economic optimization by including EPBT as constraining.

In this section, the energy modeling and optimization tool OSeMOSYS is described. In addition, it discusses LCA and its indicators and introduces the energy system modeling.

2.1 Open-Source Energy Modeling System (OSeMOSYS)

OSeMOSYS tool is specifically designed to model and computes the energy supply mix in term of generation capacity and delivery. This energy modeling tool aims to meet the energy services demands every year and in every time step of the case under study, minimizing globally the total discounted costs [17].

The merit variable to be optimized is the system total cost including the capital cost, the fixed costs, the variable costs as well as the emission penalty costs. The variable cost is related to each available capacity per technology unit, while the fixed cost goes to the maintenance of the existing capacity and the capital cost is the cost for a new addition in the capacity [16].

OSeMOSYS uses a deterministic linear optimization associated with different input data related to technical constraints, economic realities, or environmental targets and therefore assumes a unique decision-maker, perfect foresight, and competitive markets [17].

Several analysis interfaces are currently used being MoManI selected for the present work.

2.2 Energetic Sustainability Across EPBT the Frame of the Lifetime Analysis

LCA of energy generation system implies the investigation of its three indicatives to easily evaluate their sustainability and environmental performance. These indicatives are the Internal Rate of Return (IRR), Energy Payback Time (EPBT), and the Input Mitigation Potential in Term of Climate Change (IMPcc) [18]. In reality, these indicatives are evaluated separately to estimate the studied technology performances such as the entire emission activity during its entire lifetime in a cradle-to-cradle paradigm.

EPBT is considered one of the most effective unbiased estimators to evaluate the energetic sustainability of a product/process/initiative. Expressed in years, EPBT is defined as the period required for an energy generation system to produce the same amount of energy which is the primary energy that was used to produce the entire system [19]. It is

theoretically given by the cumulative energy demand; CED (MJ) over the annual energy generated by the system; E_p (MJ/year).

$$EPBT = \frac{CED}{E_p} \quad (1)$$

The CED expresses the energy input during the system's lifetime including the energy required starting from the extraction of raw materials, transportation, processing, manufacturing, and usage to the end-of-life of the activities. While E_p is the system electricity generation over a year.

2.3 EPBT Inclusion on the OSeMOSYS Tool

As explained before, the core of the presented work is to evaluate the effect of including the energetic sustainability estimator EPBT in the optimization process. For that, based on the flexibility of OSeMOSYS, EPBT can be integrated into MoManI through an accurately designed function being the main challenge convert an energetic variable into an economic cost weight.

As a first-order approximation, we will work under the hypothesis that, the energetic system must produce yearly an extra quantity of energy to recuperate the expended during the implementation process (cradle-cradle). Considering the extra production annually distributed evenly, we can define the ratio between the EPBT and the operational useful life of the energetic system as a correction factor.

The extra production will increase the corresponding yearly variable cost associated with the technology, allowing, at the same time the implementation of extra energetic capacity. Equation (2) shows the Yearly Total variable cost:

$$YTVc = \left[Pr \times \left(1 + \frac{EPBT}{OL} \right) \right] \times VC \quad (2)$$

where;

YTVc: Represents the Yearly Total Variable cost. It is the annual variable operating cost of each technology derived from the total annual by mode and the parameter variable cost;

Pr: Is the Yearly Energy Production per technology;

OL [year]: Is the Operation Life, it is the useful operational Lifetime per technology;

VC: Represents the Variable Cost and it is related to each available capacity per unit.

The effect associated with the EPBT inclusion for technology will be inversely proportional to its operational useful life. Moreover, the EPBT effect is so much less the cheaper the technology is implemented.

3 Case Study: Atlantis Power System

The proposed methodology is evaluated in a set of energetic scenarios for the Atlantis nexus. Atlantis nexus is a fictitious country developed into the MoManI interface as an example for validation and software control. Atlantis energy modeling system parameter data is fully described in Table 1.

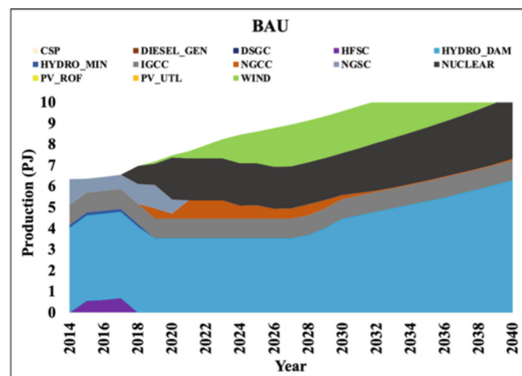
Table 1. Atlantis parameter data set.

Parameter	Output to activity ratio (Year)	Life time (Year)	EPBT (Year)	Fixed cost (M\$/PJ)	Capital cost (M\$/GW)			Capacity to activity Unit	Capacity Factor (Daily variation)		
					2014	2025	2040		D	N	
Technology											
PP1 NGSC ; Nat gas	1	30	8.17	44	2300	-	-	24.15	31.53	1	1
PP2 DSGC ; Diesel	1	30	12.68	36	900	-	-	109.50	31.53	1	1
PP3 IGCC ; Coal gasification	1	30	12.93	148	3700	-	-	11.57	31.53	1	1
PP4 HFSC ; Heavy oil	1	35	29.33	50	2300	-	-	35.67	31.53	1	1
PP5 Large Hydro	1	35	7.20	60	4000	-	-	0.0001	31.53	0.34 - 0.5	0.34 - 0.5
Mini Hydro	1	25	3.63	65	4500	-	-	0.0001	31.53	0.34 - 0.56	0.34 - 0.56
Distributed Diesel	1	40	12.68	55	1070	-	-	50.95	31.53	1	1
CSP	1	25	3.10	0	4500	-	-	46	31.53	0.28	0
PV_UTL	1	25	1.30	0	1800	-	-	8.33	31.53	0.15	0
PV_ROF	0	20	0	0	3200	-	-	8.33	31.53	0.15	0
Wind	1	25	10.32	0	1362	-	-	4.16	31.53	0.25	0.25
NGCC; NEW; Combined Cycle GT	1	35	8.17	44	1100	-	-	22.13	31.53	1	1
NEW : Nuclear (Light Water)	1	50	N. A	0	3000	-	-	13.42	31.53	1	1

3.1 Modeling Scenarios

To model the scenarios, all the parameters including technical and economical are identified from the MoManI training manual where the Atlantis power system has been modeled using OSeMOSYS [8]. For each technology, the EPBT is computed following Eq. 1.

Business As Usual (BAU). BAU is defined as a frozen version of the energetic system. The long-term evaluation of BAU allows the evaluation of the non-insertion of new initiatives into the nexus energetic mix. Figure 1 shows the yearly energy generation of the optimized technologies. Thus, the most competitive technology over the time horizon in terms of economical optimization is the Hydro dam next to the nuclear and wind technologies. Wind technology needs ten years since its introduction into the mix to reach the maximum capacity of 2 PJ. With the time horizon, nuclear production capacity increases by 70% and reaches a total of 2,400 MW on capacity integrated over the full period.

**Fig. 1.** BAU Annual energy production by technology

Effect of Applying Nuclear EPBT Values on the Energetic Mix. The first assumed scenarios are related to evaluating the effect of applying Nuclear EPBT values into the energy mix for economical optimization. Nuclear scenarios are compared with BAU to evaluate the effect of the EPBT.

Nuclear energy has been always at the center of social discussions. Probably, for this reason, EPBT cannot be precisely estimated. Because the nuclear fuel efficiency is high, only in production terms the EPBT is around 3 years. But, considering the power plant implementation as well as the waste management, the last estimations reflect a realistic EPBT between 80 and 300 years. Therefore, a set of three sub-scenarios are defined: a) Scenario with Nuclear EPBT = 20 years; b) Scenario with Nuclear EPBT = 80 years; c) Scenario with Nuclear EPBT = 300 years.

The effect of energetic sustainability on the optimization procedure for each of the defined sub-scenario is discussed following the annual energy production per technology as illustrated in Fig. 2. Indeed, Fig. 2 (b) and (c) show clearly that nuclear technology is not energetically sustainable and is not included in the energetics mix. The energy needed to be produced using the nuclear plant in BAU is now generated by the hydro dam. Even considering a short EPBT, the effect on the nuclear contribution to the energetic mixing decreases by 13% in terms of annual production capacity while additional new capacity integration is practically unnecessary (see Table 2 for details).

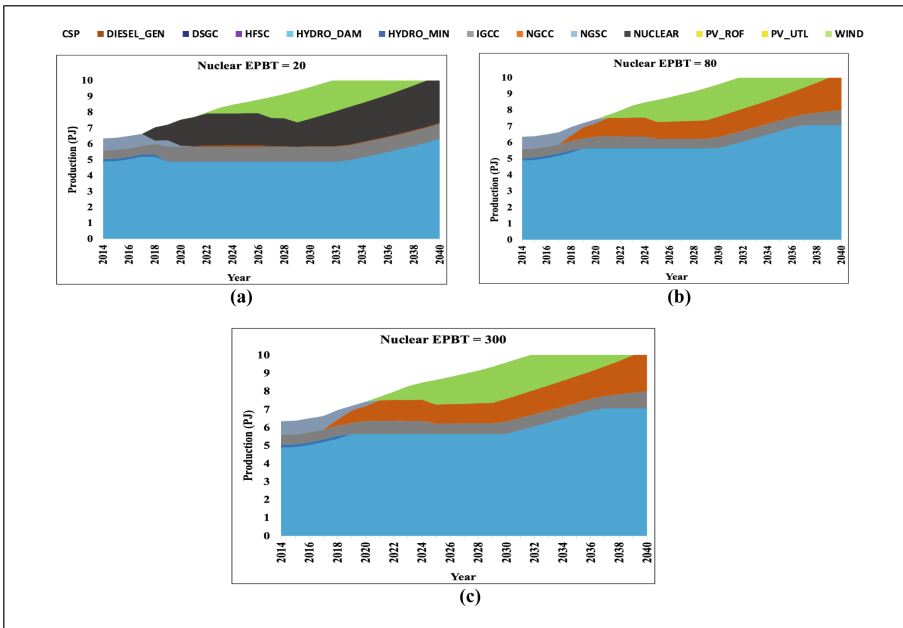


Fig. 2. Nuclear Scenarios; EPBT effect on the annual energy production by technology

Taking into account the current tendencies policymakers and experts argue toward nuclear energy that favoring the transition toward clean and safe energy without nuclear

technologies. In addition, nuclear EPBT of 50 years of a lifetime can easily reach 100 or more years due to its dismantlement operation and its waste management which cost more in terms of financial cost, energy, and environmental hazard.

However, in all scenarios, Solar Photovoltaic (PV) technology looks still not competitive being its contribution null.

Table 2. Nuclear Total annual new capacity to be installed (MW) nuclear power

Year	2014	2016	2018	2020	2022	2024	2026	2028	2030	2032	2034	2036	2038	2040
BAU	0	0	33	70	70	80	85	86	100	130	140	145	155	162
Nuclear EPBT =20 year	0	0	57	100	110	110	110	110	110	125	136	145	151	160
Nuclear EPBT =80 year	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nuclear EPBT =300 year	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Effect of Applying PV Solar EPBT Values on the Energy Mix as a Function of the Climatic Condition. Technologies cannot only be optimized depending only on their financial cost but also depend on the resource availability, especially for RE that are climatically dependent as the solar PV. Solar PV technology efficiency hardly depends on both temperature and irradiation level, increasing the corresponding capacity factor (CF) which is the percentage of the daily effective working time. Solar PV in Atlantis is modeled with a CF of 15% which cannot be considered realistic. To adequate the CF values and based on the Köppen-Geiger climate classification as used by [20], three scenarios have been defined attending to their local solar resource as shown in Table 3.

Table 3. Solar PV capacity factor under the Köppen-Geiger climate classification

	Köppen-Geiger Climate type	Calculated Capacity factor
1	Polar	35%
2	Temperate and Continental	55%
3	Tropical, Arid	95%

For each climate type, two sets of scenarios are gathered and then optimized. The first set corresponds to the standard OSeMOSYS economic optimization, while in the second set of scenarios EPBT is included in the optimization procedure. In all the cases, EPBT for nuclear technology is higher than 80 years and has not been considered.

The corresponding energetic mixing optimization via the annual production by technology is plotted in Fig. 3 (a), (c), and (e). The first notice concern eventually the PV technology which doesn't weigh in the energetic mix when considering Atlantis as a polar region, where wind, hydro, and the non-conventional technologies are more competitive.

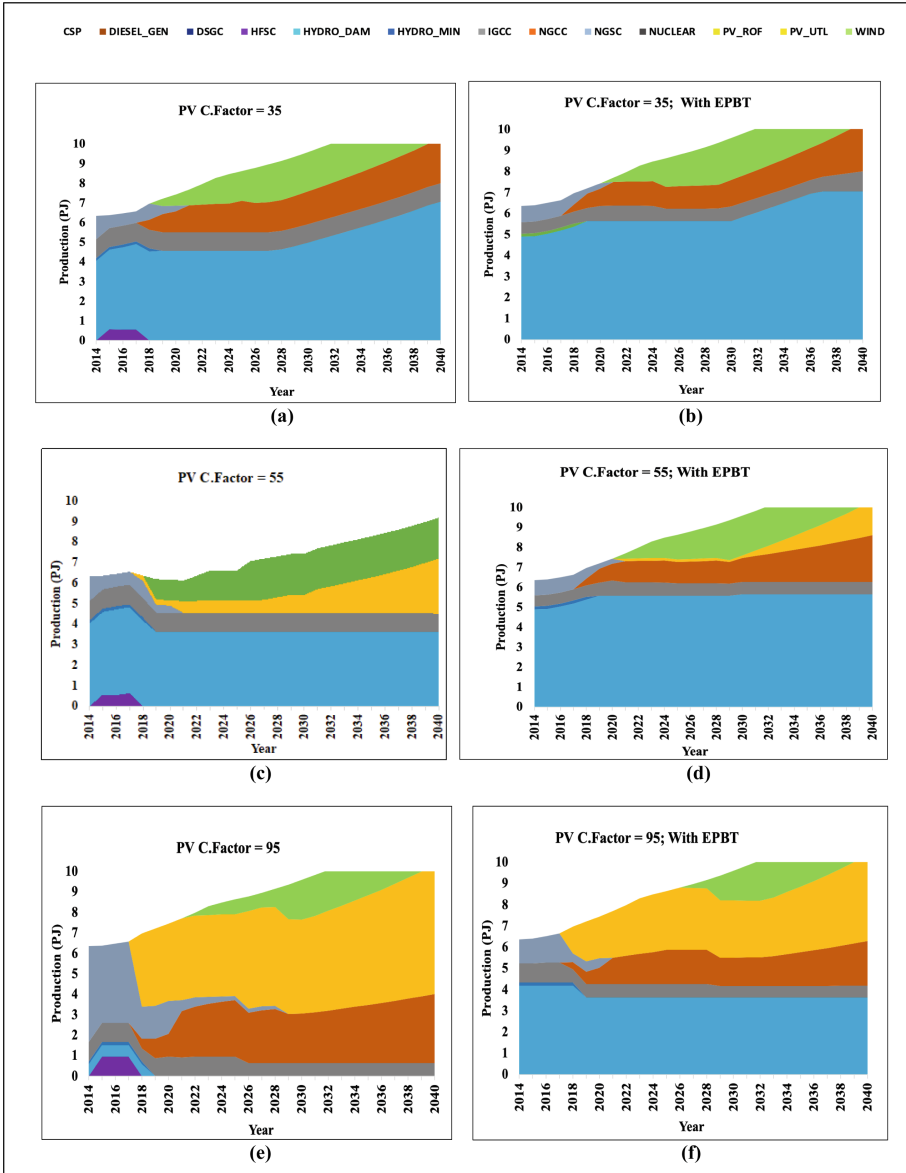


Fig. 3. Energetic mixing optimization via the annual production for different climatic condition. (a, c, e) economic optimization. In Fig (b, d, f) the corresponding EPBT is applied

Comparing the annual energy production for tropical and arid scenarios increases up to 57% more than the temperate and continental climate types.

Figure 3 (b), (d), and (f) show the same annual energetic production for the second set of scenarios when the EPBT estimator has been introduced into the optimization procedure. The EPBT value associated with the PV technology has been rudely calculated

for each climatic condition. In all the cases, the EPBT inclusion effect is a decrease of the PV contribution to the energetic mixing being, by the time horizon ending, the 40% smaller for temperate continental climate, or 34% smaller for arid conditions.

Finally, Fig. 4 shows the contributions of PV technology to a wide spectrum of climatic zones. As can be seen, the effect of forcing energy sustainability is a slower installation of new capacity. Moreover, only for strongly irradiated climatic locations, the contribution of PV technology is greater than 10% of the demand when energetic sustainability constraints are applied.

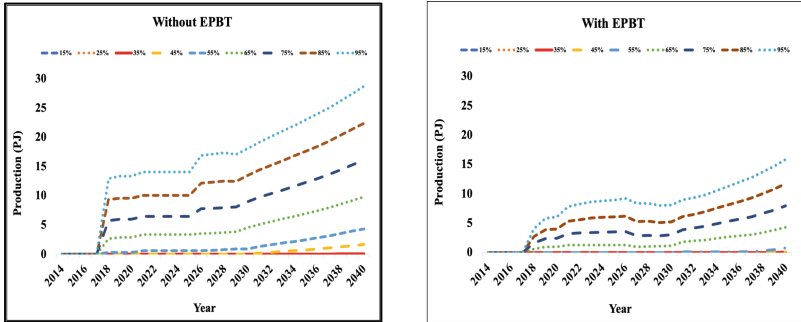


Fig. 4. Solar annual energy production scan over the capacity factor values

4 Conclusions

The effect of the implication of the energetic sustainability indicators on an optimal design of an energetic transition mix has been evaluated. The OSEMOSSYS tool (CLEWS modeling tool for EWF optimization) has been used. As a case study, the Atlantis nexus has been considered. Because OSeMOSSYS base the optimization procedures only on the economical index, a new equation, including energetic sustainability estimators (EPBT), has been designed and included in the standard tool.

Two particular cases have been studied: The effect of considering the EPBT on both nuclear and solar photovoltaic (PV) energy inclusion on the energetic mix on our target nexus Atlantis. In the case of PV, because the solar source depends on the climatic conditions, different scenarios, based on the Köppen-Geiger classification have been considered.

As a global conclusion, to ensure sustainability in the energetic transition, the inclusion of adequate estimators is crucial. More in detail, the inclusion of nuclear energy EPBT, force the not implementation of a new plant when nuclear waste management is included in the study.

Concerning the PV technology, as expected, the climatic condition is the parameter of merit to define the percentage of PV in the energetic mixing. Also, in this case, the EPBT plays an important role: because of the level of irradiation, high irradiation locations (smaller EPBT) are the best positioned. Moreover, the EPBT effect can inhibit the PV implantation in low irradiation locations, in terms of sustainability.

The developed initiatives will highly assist both developed and developing country decision-making settings toward an open and costless energy modeling system in the energetic sustainability context.

References

1. Zhang, C., Chen, X., Li, Y., Ding, W., Fu, G.: Water-energy-food nexus: Concepts, questions and methodologies. *J. Clean Prod.* **195**(6), 625–39 (2018)
2. Brouwer, F., Avgerinopoulos, G., Fazekas, D., Laspidou, C., Mercure, J.F., Pollitt, H., et al.: Energy modelling and the Nexus concept. *Energy Strategy Rev.* **19**(10), 1–6 (2018)
3. Fazekas, D., Alexandri, E., Pollitt, H.: Review of thematic models and their capacity to address the nexus and policy domains. SIM4NEXUS Report Task 1.3, European Union's Horizon 2020 research and innovation programme (2017)
4. Bechir, M.H., Mannelli, A., Agüera, A.L.: Life cycle analysis and sociocultural impact for a sustainable nexus design. In: da Costa Sanches Galvão, J.R., et al. (eds.) *Proceedings of the 1st International Conference on Water Energy Food and Sustainability (ICoWEFS 2021)*, vol. 2, pp. 670–679. Springer, Heidelberg (2021). https://doi.org/10.1007/978-3-030-75315-3_71
5. Foley, A.M., Ó Gallachóir, B.P., Hur, J., Baldick, R., McKeogh, E.J.: A strategic review of electricity systems models. *Energy* **35**(12), 4522–4530 (2010)
6. Blumsack, S., Fernandez, A.: Ready or not, here comes the smart grid! *Energy* **37**(1), 61–8 (2012)
7. Howells, M., Hermann, S., Welsch, M., Bazilian, M., Segerström, R., Alfstad, T., et al.: Integrated analysis of climate change, land-use, energy and water strategies. *Nat. Clim. Change* **3**(7), 621–6 (2013)
8. Howells, M., et al.: OSeMOSYS: The open source energy modeling system. An introduction to its ethos, structure and development. *Energy Policy* **39**(10), 5850–5870 (2011)
9. Dhakouani, A., Znouda, E., Bouden, C.: Impacts of energy efficiency policies on the integration of renewable energy. *Energy Policy* **133**(6), 0301–4215 (2019)
10. Godínez-Zamora, G., Victor-Gallardo, L., Angulo-Paniagua, J., Ramos, E., Howells, M., Usher, W., et al.: Decarbonising the transport and energy sectors: Technical feasibility and socioeconomic impacts in Costa Rica. *Energy Strategy Rev.* **32**(5), 2211–467 (2020)
11. Augutis, J., Martišauskas, L., Krikštolaitis, R.: Energy mix optimization from an energy security perspective. *Energy Convers. Manag.* **90**(11), 300–14 (2015)
12. de Moura, G.N.P., Legey, L.F.L., Howells, M.: A Brazilian perspective of power systems integration using OSeMOSYS SAMBA South America Model Base and the bargaining power of neighbouring countries: a cooperative games approach. *Energy Policy* **115**(1), 470–85 (2018)
13. Environmental Management Life Cycle Assessment Principles and Framework. International Standard, ISO 14040, 3(1) (2006)
14. Wu, P., Ma, X., Ji, J., Ma, Y.: Review on life cycle assessment of energy payback of solar photovoltaic systems and a case study. In: *Proceedings of the 8th International Conference on Applied Energy (ICAE2016)*, vol. 105, pp. 68–74. Review Energy Procedia (2017)
15. Welsch, M., Howells, M., Bazilian, M., DeCarolis, J.F., Hermann, S., Rogner, H.H.: Modelling elements of smart grids - enhancing the OSeMOSYS (Open Source Energy Modelling System) code. *Energy* **46**(1), 337–50 (2012)
16. Almulla, Y., et al.: Model Management Infrastructure (MoManI) Training Manual, KTH Royal Institute of Technology Stockholm, Sweden (2017)

17. Introduction to OSeMOSYS, <https://osemosys.readthedocs.io/en/latest/manual/Introduction.html>. Accessed 04 Feb 022
18. Howells, M., et al.: OSeMOSYS: the open source energy modeling system. An introduction to its ethos, structure and development. *Energy Policy* **39**(6), 5850–5870 (2011).
19. Fthenakis, V., Kim, H.C., Frischknecht, R., Raugei, M., Sinha, P., Stucki, M.: Life Cycle Inventories and Life Cycle Assessment of Photovoltaic Systems. PVPS, Report Task12–02, International Energy Agency, USA (2011)
20. Cabo Landeira, C.: PV systems design optimization as function of the climatic conditions. Doctoral thesis, Santiago de Compostela University, Spain (2018)



Industrial Sustainability in Southwestern Europe: A Case Study of the Possible Implementation of Biorefineries Based on Oil Seed Crops in Extremadura

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Abstract. Due to the recent encouragement by governments and international institutions to promote sustainability and green practices in industrial activities, the implantation of biorefineries has been gaining a more and more important role. Thus, they can be the perfect replacement for refineries based on crude oil, with environment-friendly processes and implying less pollution, the use of natural raw materials (even agricultural or food wastes, which are usually difficult to manage), more sustainable products, and economic development of under-industrialized regions. In that sense, Southwestern Europe (for instance, the Iberian Peninsula and specifically Extremadura, a region in Spain) has a great potential to implement green technologies, due to many factors such as suitable climate conditions (for instance, assuring many sunshine hours, which is positive for solar energy and energy crops) and a considerable agricultural tradition. The aim of this study was to assess the possibility of the implementation of a biorefinery based on oil seed crops in Extremadura, paying attention to the main raw materials used and the possible processes included to produce a wide range of products such as biomass, cake for animal feed, vegetable oil, biodiesel, glycerol or biolubricants (for different industrial purposes), among others. As a result, a global process with a high atom efficiency was presented, obtaining good yields (exceeding 95 and 90% for biodiesel and biolubricant production, respectively). In conclusion, a biorefinery of these characteristics (or similar) would be feasible in this region, mainly due to the high yield and quality of the products obtained.

Keywords: Biomass · Biodiesel · Biolubricant · Glycerol · Vegetable oils

1 Introduction

In the twenty-first century, the transition from a linear economy based on fossil fuels to a circular bioeconomy (whose underlying principle is the emission of zero waste)

is no longer an option, but an imperative, given global concern about the depletion of fossil resources and the demand for eco-compatible innovative products. Biorefinery is an indispensable technology to implement the circular bioeconomy project since it produces value-added products (from different sources of biomass, such as waste from agricultural, forestry, livestock, industrial, etc.), such as biofuels, chemicals, energy, food and other bio-based products. Therefore, it can be concluded that the most suitable areas to implement biorefineries are those in which abundant agricultural waste is generated. For this reason, Extremadura, located in the southwest of Spain, would be an ideal region for the development of biorefineries due to its strong agricultural and livestock character.

Therefore, considering the above, the main objectives on which this article focuses are the production of biofuels (biodiesel and biolubricant) from biomass and the feasibility of implementing a biorefinery in Extremadura.

2 Materials and Methods

Some of the aspects covered in this work were studied at a laboratory level (biodiesel and biolubricant production). A Batch system was used to synthesize biodiesel (fatty acid methyl esters, FAMES). It consists of a reactor equipped with heating, temperature control, agitation and condensation systems.

Once biodiesel has been obtained, a transesterification reaction between oil and a short-chain alcohol (methanol) in the presence of a catalyst, it was purified (by means of different washes) and dried (to remove possible moisture residues). Subsequently, a series of parameters were analyzed especially methyl ester content by gas chromatography and oxidation stability by the Rancimat method. Finally, the result obtained, from each of them, was evaluated according to the requirements of Standard UNE EN 14,214 [1], which specifies all relevant characteristics, requirements and test methods for FAMES.

The production of biolubricant was carried out in a similar equipment. The differences are that this equipment had a Dean Stark collector and a vacuum pump.

The biolubricant obtained, by transesterification between biodiesel and a complex alcohol in the presence of a catalyst, was purified and subsequently, like biodiesel, was characterized following the same procedure. Details of the experimental systems used and the methodology applied can be found in previous publications [2–5].

3 Results and Discussion

3.1 Biomass

Biomass means all organic matter capable of being transformed into bioenergy or bio-products. Biomass can be obtained from agriculture, forestry, livestock, or from industries associated with these sectors (agro-food, forestry, aquaculture, among others). Biomass is also considered the organic fraction of municipal waste. Biomass can be energetically recovered through various thermochemical and/or biological processes to obtain bioenergy in the form of electricity, heat or biofuels for transport such as biodiesel, bioethanol, etc. [6].

The conversion of thermochemical-based biomass includes several methods, such as combustion, gasification and pyrolysis. Although combustion is the simplest method for biomass conversion, it is not environmentally friendly, mainly due to carbon dioxide, carbon monoxide and solid particle emissions. In addition, it is associated with technical difficulties such as ash management. Gasification is a more efficient bioenergy conversion method compared to combustion; However, its application is limited as it requires a large capital investment and leads to gas production that must be used immediately to minimize storage and transportation costs. Pyrolysis is an effective technique for the thermochemical conversion of biomass and waste materials into energy products. Currently, it is used for the production of bio-oil and the generation of other valuable chemical by-products [7].

In Extremadura, the biomass sector has grown considerably in recent years, mainly due to the price difference between conventional fuels and biomass. For this reason, installations with significant thermal consumption have made the switch to biomass, obtaining low return on investment periods. In the national context, on the power accumulated by regions in Spain, Extremadura is in fourth place after Andalusia, Castile and León and Catalonia, whereas in power installed by inhabitants, it occupies third place, which gives an idea of the importance that this biofuel can take in our region.

3.2 Biodiesel

Biodiesel, an alternative and liquid biofuel to reduce dependence on fossil fuels [8], is made from different sources of biomass, among which oil crops are the most important, that is, crops that produce seeds rich in vegetable oils, such as safflower (*Carthamus tinctorius*), rapeseed (*Brassica napus L.*), sunflower (*Helianthus agnus L.*) and soy (*Glycine max*). Other non-conventional oilseed crops include Ethiopian rapeseed (*Brasica carinata*), which is highly resistant to drought and pests, cardoon (*Cynara cardunculus*), a Mediterranean species with a high biomass production capacity, and *Jatropha curcas* with capacity to grow in sandy soils of low fertility and in areas with low rainfall.

Biodiesel can be obtained from different biomass conversion processes such as pyrolysis, transesterification, dilution and microemulsification. Low calorific value, low engine performance, instability and low-quality biodiesel produced by pyrolysis, microemulsification and dilution process have made it unsuitable for commercial energy production. Alternatively, it is observed that transesterification is the best process for the generation of commercial biodiesel of high quality and quantity. Transesterification, to obtain biodiesel, consists of the reaction between triglycerides (vegetable oil) and low molecular weight alcohols, in the presence of a catalyst, which produce methyl esters of fatty acids (FAMES) and glycerol as a byproduct [9]. Below is shown, in a generic way, the global equation of this reaction (see Fig. 1).

Biodiesel production and consumption have expanded rapidly as the best short-term substitute for mineral diesel. Biodiesel production reached 46.7 million cubic meters worldwide in 2019, and follows a growing trend in the future [10], as it has several advantages compared to petrodiesel, including the absence of aromatic compounds, absence of sulphur, non-toxicity, renewal capacity and high flash point. For this reason, in recent years, different studies [5, 11] have been carried out in which the main objective has been to obtain biodiesel with a similar performance to mineral diesel. For this, starting

from the raw material, mentioned above, and by transesterification, whose operating conditions have been FAMES:Alcohol mole ratio: 1:6, catalyst concentration: 1.5%, temperature: 65 °C and reaction time: 120 min, different types of biodiesel have been obtained (in all cases a conversion greater than 95% has been achieved). Subsequently, for each of them a series of parameters has been measured such as viscosity, density, oxidation stability, viscosity index, acidity index, flash point and combustion, etc., and then, the values obtained have been compared with the limits set by UNE EN 14,214. In all cases, most of the requirements have been met, except for the oxidation stability value that has only been achieved with biodiesel obtained from high oleic safflower.

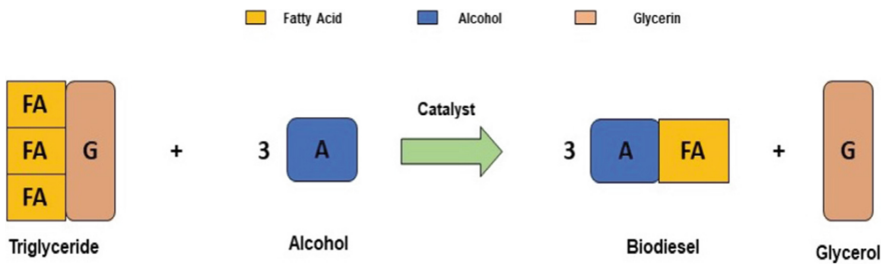


Fig. 1. Production of Biodiesel via transesterification reaction [9].

Biodiesel is also used as an intermediate product for the production of biolubricants as it will be commented in the following section.

3.3 Biolubricant

Biolubricants are biologically based lubricants, alternative to mineral oils because they possess certain natural and biodegradable properties [12]. They can be obtained from different routes of chemical modification of vegetable oils (see Fig. 2).

The processes used to obtain biolubricant as the final product are based on a series of basic reactions that include ring opening, esterification, hydrolysis and transesterification. These reactions combine to produce the following chemical pathways (see Fig. 2):

- Route I begins with a hydrolysis reaction (process by which hydrogen is added to the double bonds in the triglycerides of an oil molecule) of the vegetable oil, resulting in the formation of free fatty acids (FFA) as a product, plus glycerol as a by-product. Subsequently, the esterification (process by which an ester is synthesized) of the FFA is carried out, using an upper alcohol, usually provided with several hydroxy groups (polyol).

- Route II consists of the transesterification of methyl esters (FAMES or biodiesel) with a polyol or superior alcohol (this is a reaction in which an ester is formed through the exchange of the alkyl group). During the reaction transesterification releases some of the residual methanol contained in biodiesel.

- Route III takes place in two stages. In the first stage, the transesterification of vegetable oil with methanol takes place producing methyl esters of fatty acids (FAMES or biodiesel) as a product and glycerol as a by-product. During the second stage, the same procedure is developed as on route II.
- Route IV is divided into two steps. The first step coincides with the first stage of Route III. The second step consists of epoxidation (oxygen transfer reaction applied to a number of types of olefins to form epoxides) of the FAMES produced, with hydrogen peroxide and acetic acid.
- Route V begins with the epoxidation of the vegetable oil followed by the opening of the epoxy ring by alkolysis or hydrolysis.
- Finally, it is noted that route VI consists only of epoxidation reactions in vegetable oils. The epoxidated oil, in this route, is considered the biolubricant.

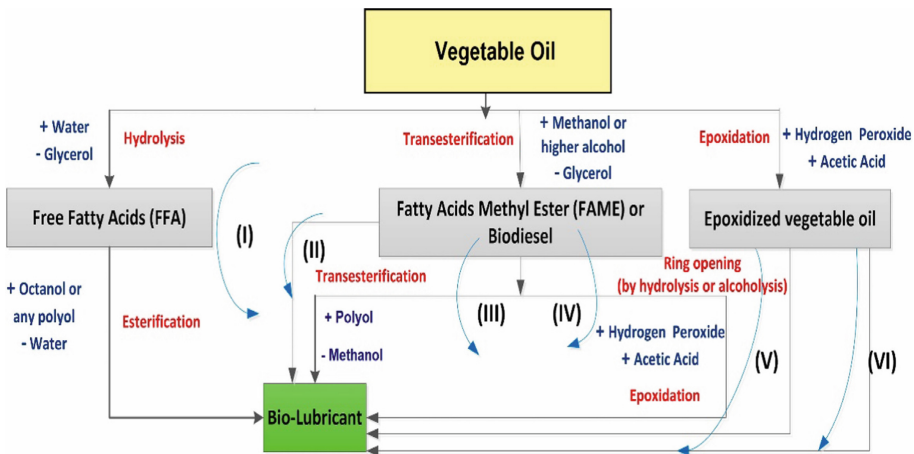


Fig. 2. Different routes of chemical modification of vegetable oils to obtain biolubricants [13].

The most commonly used route to obtain biolubricants, according to the literature, is a double transesterification (Route III). Table 1 shows different studies in which this method has been followed.

Different studies have been carried out to obtain biolubricants. For their production, different raw material and different types of alcohol were used. In turn, different operating variables have also been set for each study, such as different temperatures, between 130 and 170 °C. The molar ratio, as it can be seen in the table, was changed depending on the alcohol used. Catalyst concentration is another variable that has been modified (between 1% and 1.5%). It can also be seen that, in some studies, vacuum has been used (which favors the removal of methanol). Finally, reaction times were between 60 and 120 min. As a conclusion, it can be observed that all the studies showed a conversion above 90%. This is quite significant, as it indicates that a biolubricant of high purity can be possible.

Today, around 50% of the world's mineral lubricants end up polluting the environment. In addition, one third of the particulate emissions from diesel engines are due to

Table 1. Different biolubricants and their chemical conditions (Catalyst concentration, [Cat.]; temperature, T; pressure, P; time, t) [2–4, 12, 14].

Raw material	Alcohol	Alcohol: FAME ratio	[Cat.], %	T, °C	P, mmHg	t, min	Yield, %
Cardoon	2,2-dimethyl-1,3-propanediol	1:1	1.5	130	760	120	92.76
Frying oil	2-ethyl-1-hexanol	1/3:1	1.5	170	760	60	96.80
High oleic safflower	2-ethyl-2-hydroxymethyl-1,3-propanediol	1:1	1.5	140	360	90	92.90
	Pentaerythritol	1/3:1	1.0	160	260	120	94.13
Rapeseed	2-ethyl-1-hexanol	1/3:1	1.5	170	760	60	96.60
	2-ethyl-2-hydroxymethyl-1,3-propanediol	1:1	1.5	120	360	90	99.41
Seed	2-ethyl-1-hexanol	1/3:1	1.5	170	760	60	97.10

the evaporation of the lubricant. For this reason, the production and use of biolubricants has increased to overcome these disadvantages.

3.4 Biorefineries

Taken into account the previous section, in order to maximize biomass utilization and minimize waste and emissions associated with the conversion of bioenergy products, the concept of biorefinery was proposed [15]. This concept was used to efficiently produce high-value products from different raw materials such as lignocellulosic biomass, algae, food waste, microbial treated waste and fertilizers. Recently, enzyme technologies with biorefineries have also been developed and integrated to generate advanced biofuels. The notion of using biomaterials in technical and production cycles in addition to the biological cycle opens the opportunities for reuse, recycling and remanufacture known as circular bioeconomy.

The circular bioeconomy, defined by the European Commission in 2018, promises to mitigate the effects of climate change while providing a source of renewable carbon (biomass) and creates commercial and employment opportunities, especially in rural areas.

Looking ahead, it is expected that most of the economy / global industry will gradually become a sustainable bio-based society that has bioenergy, biofuels and bio-based products as main foundations and bio-refineries as a basis. Such replacement of oil for biomass will require some radical changes in the current production of goods and services: the biological and chemical sciences will play a leading role in the generation of future industries and new synergies of biological, physical, chemical and technical sciences must be enhanced.

A graphic example of a biorefinery based on vegetable oils is shown in Fig. 3:

In a biorefinery, various processes are carried out (see Fig. 3), in which different products are obtained (biodiesel and biolubricant) and by-products (glycerol and methanol). In addition to these processes, it can be observed that residues such as the seed shell,

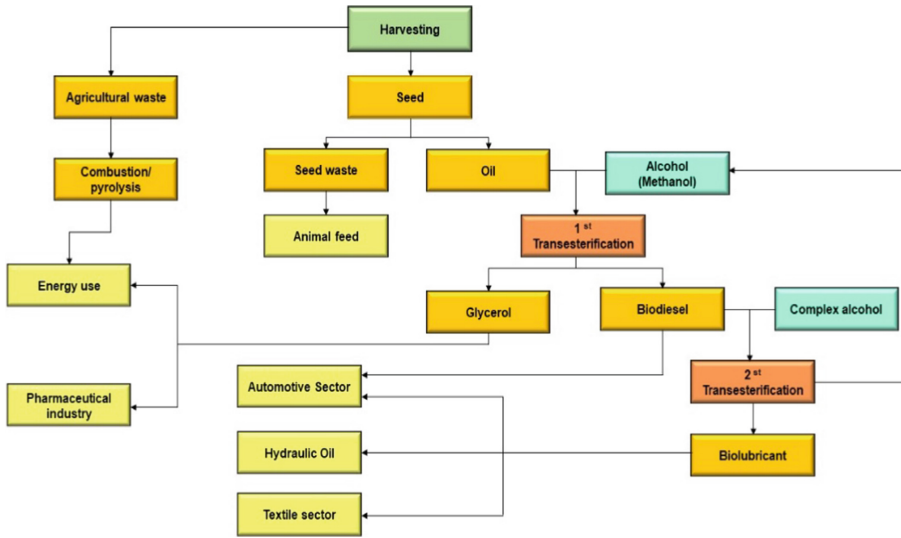


Fig. 3. Example of processes carried out in a biorefinery.

from which the starting oil is extracted for the production of biodiesel, can be used to make cake for the livestock sector. Also, agricultural waste, such as straw, etc., can also be used as raw materials for combustion processes and pyrolysis. In turn, the energy generated during combustion or pyrolysis can also be used for different purposes. On the other hand, it can be seen that methanol released during the second transesterification reaction (biolubricant production) can be recovered and reused as a reagent in the first transesterification (biodiesel production), and glycerol, obtained as a product in the first transesterification, can be used as a material for energy use, biomedical applications, materials for batteries, sensors and solid-state electrolytes. Finally, the biolubricant can be used for different uses in textile, automobile (like biodiesel) or hydraulic sectors, among others.

Currently, there are already operational biorefineries based on simple raw materials, however, the final objective would be to develop industrial facilities in Spain that, from different raw materials, generate multiple products including energy and biomass-based chemicals (building blocks and their chemical platforms). In this last aspect, the region of Extremadura could be an ideal area to implement biorefineries, for different reasons [16]:

- It has a marked agricultural and forestry character. The huge quantities of waste from activities in this sector are considerable, which can therefore be a source of energy use.
- It is the fourth useful agricultural area in Spain, with 2.5×10^6 hectares, representing almost 11% of the total useful agricultural area of this country. In this way, the use of biomass and agricultural waste to create value-added products could be extensive in a region with such a long agricultural tradition.

- Due to their variety of agricultural production, different kinds of biorefineries could be feasible in this region, depending on the raw material on which they are based. This ensures a great diversification and adaptation to the different markets, making stable the economic development of this region.
- Extremadura has the fourteenth (of seventeen) gross domestic product per capita, with 19,386 € (well below the national average, 25,410 €). Therefore, the implementation of biorefineries could be a good way to develop poor areas in a sustainable way.
- Its privileged location in the Iberian Peninsula could make the marketing of manufactured products possible; as it is among important industrial areas such as Lisbon, Madrid or Seville. Consequently, the production of biorefineries could have regional, national and international business objectives, which could make the size of biorefineries variable.

4 Conclusions

- Biomass can be valued energetically through different thermochemical and/or biological processes to obtain bioenergy as electricity, biofuels, etc.
- Biofuels, such as biodiesel and biolubricants, are obtained from different biomass sources, usually oilseed crops, through different conversion processes. The most common, for both, is a transesterification reaction, obtaining high products yields and proving their feasibility.
- The region of Extremadura, due to its strong agricultural and forestry character and its location in the Iberian Peninsula, is an ideal area to implement biorefineries, promoting its economical growth in a sustainable way.

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References

1. UNE-EN.: UNE-EN 14214:2013 V2+A2 Norma Española Productos petrolíferos líquidos Ésteres metílicos de ácidos grasos (FAME) para motores diésel y equipos de calefacción Requisitos y métodos de ensayo, 6 (2019)
2. Nogales-Delgado, S., Encinar, J.M., González Cortés, Á.: High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production. *Ind. Crops Prod.* **170**, 113701 (2021)
3. Encinar, J.M., Nogales, S., González, J.F.: Biodiesel and biolubricant production from different vegetable oils through transesterification. *Eng. Rep.* **2**(12), 1–10 (2020)
4. Encinar, J.M., Nogales-Delgado, S., Pinilla, A.: Biolubricant production through double transesterification: Reactor design for the implementation of a biorefinery based on rapeseed. *Processes* **9**(7) (2021)

5. Nogales-delgado, S.: Industrial Crops & Products High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production e María Encinar *, Alvaro Gonz a. 170 (2021)
6. Gregorio, M.De.: Estudios sobre la Economía Española - 2020/01 Biomasa en España. Generación de valor añadido y análisis prospectivo. (2020). <http://documentos.fedea.net/pubs/eee/eee2020-01.pdf>
7. Wang, Y., Akbarzadeh, A., Chong, L., Du, J., Tahir, N., Awasthi, M.K.: Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: a review. *Chemosphere* [Internet]. **297**(March), 134181 (2022). <https://doi.org/10.1016/j.chemosphere.2022.134181>
8. Amjith, L.R., Bavanish, B.: A review on biomass and wind as renewable energy for sustainable environment. *Chemosphere* **293**(January), 133579 (2022). <https://doi.org/10.1016/j.chemosphere.2022.133579>
9. Topare, N.S., Jogdand, R.I., Shinde, H.P., More, R.S., Khan, A., Asiri, AM.: A short review on approach for biodiesel production: Feedstock's, properties, process parameters and environmental sustainability. *Mater. Today Proc.* **2021** (2021). <https://doi.org/10.1016/j.matpr.2021.12.216>
10. Zhang, J., Wang, Y., Muldoon, VL., Deng, S.: Crude glycerol and glycerol as fuels and fuel additives in combustion applications. *Renew. Sustain. Energy Rev.* **159**(January), 112206 (2022). <https://doi.org/10.1016/j.rser.2022.112206>
11. Encinar, J.M., Nogales, S., González, J.F.: The effect of BHA on oxidative stability of biodiesel from different sources. *Greenhouse Gases Sci. Technol.* **10**(6), 1193–1201 (2020)
12. Encinar, J.M., Nogales-Delgado, S., Álvarez-Medina, C.M.: High oleic safflower biolubricant through double transesterification with methanol and pentaerythritol: Production, characterization, and antioxidant addition. *Arab. J. Chem.* **15**(5), 103796 (2022)
13. Negi, P., Singh, Y., Tiwari, K.: A review on the production and characterization methods of bio-based lubricants. *Mater. Today Proc.* (2021). <https://doi.org/10.1016/j.matpr.2020.12.1211>
14. Nogales-Delgado, S., Encinar Martín, J.M.: Cardoon biolubricant through double transesterification: Assessment of its oxidative, thermal and storage stability. *Mater. Lett.* **302** (2021)
15. Cherubini, F.: The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers. Manag.* **51**(7), 1412–1421 (2010). <http://dx.doi.org/10.1016/j.enconman.2010.01.015>
16. Nogales-Delgado, S., Sánchez, N., Encinar, J.M.: Valorization of cynara *Cardunculus L.* Oil as the basis of a biorefinery for biodiesel and biolubricant production. *Energies* **13**(19), 5085 (2020)



Characterization and Feasibility of Fruit Tree Pruning for Energy Use

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Abstract. Extremadura region (Spain) produces more than 44,000 hectares of fruit trees. It is the leading autonomous community in plum production and the fourth in peach production. Its cultivation generates significant amounts of pruning that are not used. In this work, a characterization of different types of fruit tree prunings and a study of the necessary pre-treatments for their energy-efficient use are carried out. Samples of four types of fruit tree (plum (*Prunus domestica*), peach (*Prunus persica*), loquat (*Eriobotrya japonica*) and nectarine (*Prunus persica* var. *nucipersica*)) were subjected to a series of analyses to determine their energy properties as a biofuel. In addition, the different samples were subjected to a series of pre-treatments, such as drying and chipping. The results showed that, in general, pruning residues can be used in the form of chips in medium and large thermal equipment, as their ash content impedes their efficient use in small domestic equipment. Among the samples analyzed, plum tree prunings have slightly better characteristics than the other fruit tree prunings studied.

Keywords: Fruit-tree pruning · Biomass · Thermal use · Characterization

1 Introduction

In Spain, there are extensive agricultural areas in which significant quantities of waste are generated as a result of the normal development of the activity. Although important advances have been made in the management of certain biomass waste, there are no global solutions applicable to all of them and, even today, certain by-products can still generate environmental problems if they are not managed appropriately. This is the case of fruit tree waste.

The Spanish fruit and vegetable sector is of great importance to the country's economy. According to data from the European Statistical Office EUROSTAT, Spain was the country with the largest area of fruit trees in the European Union in 2017. Spain accounted for 33% of a total of 1,409,000 ha of fruit trees in the EU (422,800 ha). At a considerable distance behind were Italy and Poland, with 22 and 13%, respectively.

Specifically, the Autonomous Community of Extremadura has a total of 44,042 ha of cultivated fruit trees. It is the leading Autonomous Community in plum production (78,500 t) and fig production (18,755 t), third in walnut production and fourth in

peach production. The latter is the most cultivated fruit species in Spain, with a total of 84,000 ha, of which just over 9,000 ha (11%) are in Extremadura and provide an annual production of 146,153 t [1].

In the management of pruning waste, field burning without energy recovery has traditionally been the most widespread procedure. This option causes carbon dioxide emissions into the atmosphere, loss of organic matter in agricultural systems and fire hazards. Another problem is that to carry out controlled burning, the pruning residues must first be accumulated and left to dry for some time on the farm, which leads to the appearance of pests.

As an alternative, revaluation as biofuel can be considered, for which pruning residues are subjected to a series of pre-treatments until they are suitable for energy use.

The use of biofuels in agricultural activities today has many advantages, not least of which is that their use does not imply a reduction in agricultural land [2]. In addition to this, the continuous increase in the use of biofuels to meet energy demand has led biomass companies to start looking for new products, such as residues from agricultural and agro-industrial activities and their combinations [3, 4].

Concerning the use of waste as biomass, although there are numerous references in the field of forestry residues [5, 6], this is not the case for the use of agricultural crop residues in general and fruit pruning residues in particular. In this respect, the results obtained in the EuroPruning and uP_Running projects, coordinated by the Centre for Research on Energy Resources and Consumption (CIRCE), should be highlighted. These projects demonstrated the technical, economic, social and environmental feasibility of using certain agricultural prunings for energy purposes, which is in line with the objectives of this work. The quantification of prunings, as well as collection logistics, have been the main focus of these projects [7].

In this work, an energy characterization of prunings from different fruit trees and a study of several necessary pre-treatments (drying and chipping) are carried out so that they can be used as biofuels in small thermal generation equipment.

2 Materials and Methods

2.1 Biomass Characterization

All samples used were collected from the soil after winter pruning of fruit trees in the area of Badajoz (Spain). The collected samples are composed of fruit tree branches less than 2 cm thick. The varieties analyzed, the most common in the area, were those indicated in Table 1.

Characterization analyses were carried out on all the samples listed in Table 2, according to the corresponding standards.

Fixed carbon is calculated on a dry basis by subtracting volatile matter and ash content from 100.

2.2 Drying Tests

Drying tests for fruit tree pruning were carried out through a convective dryer (CE130, Gunt Hamburg), composed of four removable stainless steel trays, a drying channel (to

Table 1. Types of fruit trees used in the work.

Fruit tree pruning
Plum tree (<i>Prunus domestica</i>)
Peach tree (<i>Prunus persica</i>)
Nectarine tree (<i>Prunus persica</i> var. <i>nucipersica</i>)
Loquat tree (<i>Eriobotrya japonica</i>)

Table 2. Standards used in the analyses carried out.

	Standard
Moisture	UNE-EN ISO 18134-2:2017 [8]
Volatile matter	UNE-EN ISO 18123:2016 [9]
Ash	UNE-EN ISO 18122:2016 [10]
Calorific value	UNE-EN ISO 18125:2018 [11]
Bulk density	UNE-EN ISO 17828:2016 [12]
Carbon, hydrogen, nitrogen	UNE-EN ISO 16948:2015 [13]
Sulphur, chlorine	UNE-EN ISO 16994:2017 [14]
Sodium, potassium	UNE-EN ISO 16967:2015 [15]

heat the product and remove moisture), flow control through a heatable fan, and a digital balance to record weight loss.

Around 250 g of waste was spread on each of the four trays (1 kg in total), so that the thickness of the sample on each tray was less than 1 cm. Several tests were carried out, with different drying air velocities ($v = 0.8, 1.2$ and 1.6 m/s) and temperatures ($T = 30, 40$ and 50 °C). Tests that were carried out are shown in Table 3.

Table 3. Drying test carried out.

	FTP1	FTP2	FTP3	FTP4	FTP5	FTP6	FTP7	FTP8	FTP9
v (m/s)	0.8	0.8	0.8	1.2	1.2	1.2	1.6	1.6	1.6
T (°C)	30	40	50	30	40	50	30	40	50

Through experimental tests, the moisture ratio was obtained. Using Fick's diffusion equation for flat geometry, the characteristic dimension and properties of the product, effective diffusivity, and activation energy parameters were calculated.

Effective diffusivity is a fundamental parameter in drying processes. Using experimental tests, it is possible to obtain the moisture ratio, MR, by direct taking. The variation

of this ratio is closely associated with Fick's diffusion equation. The analytical solution of Fick's second law for flat geometry and long periods y MR values < 0.6 [16, 17] can be simplified and obtain Eq. 1:

$$MR = \frac{8}{\pi^2} \cdot \exp\left(-\frac{\pi^2 D_{eff} t}{L^2}\right) \quad (1)$$

where D_{eff} is the effective diffusivity (m^2/s), L is the characteristic dimension of the "thin layer" product (m), and t is the drying time (s).

To determine the effective diffusivity in the studied byproduct, drying analysis was carried out for various temperatures (30 °C, 40 °C and 50 °C) and different inlet airflow (0.8 m/s, 1.2 m/s and 1.6 m/s) in the convective dryer previously mentioned.

The activation energy, E_a , is the minimum energy required to produce a chemical reaction. In this case, is the minimum energy required to start the drying process. Generally, activation energy and pre-exponential factor are been considered constant. If the values of LN (D_{eff}) versus $1/T$ (K^{-1}) are represented, it is possible to identify them by a linear relationship in the temperature range selected. The value of the slope of the line represented coincides with the value of E_a/R . So that it can obtain the values of the activation energy of the byproducts studied.

2.3 Chipping Tests

To compare different methods of particle size reduction, several chipping trials were carried out with two different chippers: a blade chipper and a roller mill.

Table 4 shows the characteristics of the equipment used.

Table 4. Characteristics of the chipping equipment used.

	Model	Weight (kg)	Engine	Nominal Power (kW)
Blade chipper	Cip Line B25 E4	170	Three-phase asynchronous	4
Roller mill	GeoTech ESB 2803 Roller	30	Single-phase	2.8

Three types of tests were carried out, one with the blade chipper and two with the roller mill. In the second case, one test was carried out with the minimum aperture and the other with the maximum aperture. A determined amount of sample was manually introduced into the equipment, and the time of the test and the power consumption of the equipment was recorded with a network analyzer.

3 Results and Discussion

3.1 Biomass Characterization

Table 5 shows the results of the proximate analysis of the samples used in this study.

Table 5. Proximate analysis.

Fruit tree pruning	Volatile matter (% db)	Fixed carbon (% db)	Ash (% db)	Moisture (% wb)
Plum tree (<i>Prunus domestica</i>)	84.88	11.27	3.85 ± 0.15	29.64 ± 4
Peach tree (<i>Prunus persica</i>)	82.48	15.05	2.47 ± 0.4	35.31 ± 0.5
Nectarine tree (<i>Prunus persica</i> var. <i>nucipersica</i>)	82.74	13.81	3.45 ± 0.3	45.02 ± 0.6
Loquat tree (<i>Eriobotrya japonica</i>)	78.60	17.16	4.24 ± 0.5	53.31 ± 0.5

Moisture varies depending on the time the samples have been collected and the weather conditions. In this case, pruning was carried out in December and all moisture analysis was done two days after collection.

Given the results shown in Table 5, it can be seen that the ash percentage of the samples is slightly high in all cases. This situation will harm the use of these by-products in small thermal equipment with a minimum ash collection capacity. In this sense, it is recommended to use them in higher power equipment in the tertiary or industrial sector, with an acceptable capacity to be able to manage the ash adequately. In addition, the ash percentage data are very close to those shown for other species used for thermal use, such as miscanthus or switchgrass [18, 19]. However, the pruning of plum trees with larger branches has a lower percentage of ash, as it has a lower proportion of bark in its composition. In this respect, it would be recommended for thermal use compared to other options.

Both volatile matter and fixed carbon values are similar to each other and very similar to other similar by-products.

Table 6 shows the results of the elemental analysis performed on the samples. No significant variations from typical lignocellulosic biomass pruning values are observed.

Table 7 compiles the values of bulk density and high heating values for all samples.

Taking into account the bulk density, if the effect of moisture weight is eliminated, it can be indicated that plum prunings have the highest bulk density (dry basis), reaching approximately 141 kg/m³, as opposed to loquat (dry basis) with 119 kg/m³.

The high heating values indicate the similarity between them, as all samples are made up of small fruit tree branch prunings. There are slight variations between the different types, but these are not significant. This fact leads to the conclusion that the calorific value of the samples analyzed is not a differentiating factor in favor of one of the options.

Table 6. Ultimate analysis.

Fruit tree pruning	C (% db)	H (% db)	N (% db)	S (% db)	Na (% db)	K (% db)	Cl (% db)
Plum tree (<i>Prunus domestica</i>)	44.51	7.01	0.28	0.03	0.028	0.082	0.039
Peach tree (<i>Prunus persica</i>)	45.82	7.14	0.45	0.02	0.005	0.233	0.096
Nectarine tree (<i>Prunus persica</i> var. <i>nucipersica</i>)	45.82	7.14	0.45	0.02	0.005	0.274	0.015
Loquat tree (<i>Eriobotrya japonica</i>)	45.06	7.01	1.31	0.05	0.005	0.219	0.130

Table 7. Bulk density and High Heating Value.

Fruit tree pruning	Bulk density (% ar)	HHV (kcal/kg)
Plum tree (<i>Prunus domestica</i>)	194.50 ± 30	4217
Peach tree (<i>Prunus persica</i>)	201.11 ± 30	4223
Nectarine tree (<i>Prunus persica</i> var. <i>nucipersica</i>)	231.02 ± 30	4260
Loquat tree (<i>Eriobotrya japonica</i>)	255.83 ± 30	4252

3.2 Drying Tests

Due to the similarity of characteristics between the different samples, it was decided to carry out the drying tests (as well as the chipping tests) using only plum prunings. The pruning of this fruit tree was considered to be the most representative, since there are larger quantities available, as it is the most widespread crop of this type in the Autonomous Community of Extremadura. In addition, it is the type of fruit tree that is maintained in the area, as the other varieties are disappearing because the plum is a fruit that is less dependent on seasonality, being more interesting to produce than the others.

Figure 1 shows the moisture ratio concerning drying time for each of the temperatures and air flows studied.

As expected, drying of fruit tree pruning (FTP) is produced in a shorter period of time the higher the temperature of the experiment is. For the same temperature, the drying process is slower the lower the airflow is. In this way the highest speed in the decrease in moisture ratio is achieved in the FTP9 test, obtaining the lowest value in the FTP1 test.

The values of D_{eff} and $\text{LN}(D_{\text{eff}})$ are shown in Table 8. Comparing D_{eff} values obtained in this work with those suggested by other authors for other agricultural by-products

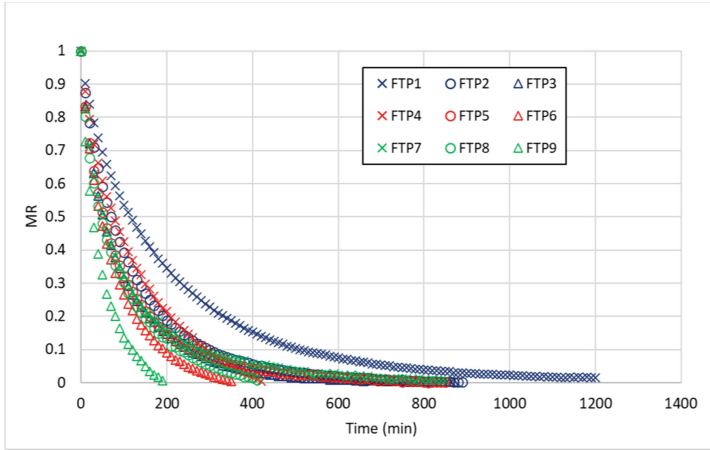


Fig. 1. Moisture ratio MR vs drying time.

[20, 21], the olive mill by-products, for example, present values, in natural convection at 40 °C, about $2.1 \cdot 10^{-10}$ for olive pomace, about $1.1 \cdot 10^{-10}$ for olive sludge and about $4.1 \cdot 10^{-10}$ for olive mill wastewater [20, 21].

Table 8. Effective diffusivity and its LN.

	D_{eff}	$LN(D_{eff})$
FTP1	2.82955E-09	-19.683149
FTP2	6.34411E-09	-18.87574
FTP3	5.71668E-09	-18.979878
FTP4	9.01462E-09	-18.524418
FTP5	6.23831E-09	-18.892556
FTP6	1.37035E-08	-18.105612
FTP7	4.85644E-09	-19.142959
FTP8	8.62744E-09	-18.568318
FTP9	1.8065E-08	-7.829288

The value of the slope of the line represented by $LN(D_{eff})$ and $1/T (K^{-1})$ coincides with the value of E_a/R . Thus, it is possible to obtain the values of the activation energy of the byproduct studied. These values are shown in Table 9.

E_a values obtained by other authors for agricultural by-products are, in kJ/mol: olive pomace 91.35 [20], olive sludge 14.04 [20], olive mill wastewater 77.15 [20] or vegetable waste 19.82 [17], for example.

Table 9. Activation energy (kJ/mol).

For 0.8 m/s	For 1.2 m/s	For 1.6 m/s
29.0250054	16.549017	13.4074732

3.3 Chipping Tests

Figure 2 shows the results for the different chipping operations carried out.



Fig. 2. Resulting product. Blade chipper (left), roller mill: minimum aperture (centre), maximum aperture (right).

The chips resulting from the blade chipper have a smaller and more homogeneous grain size than the others. It can be considered the sample that achieved the highest quality considering its size and particle size distribution.

From the tests carried out with the roller mill, the particle size was approximately the same in both cases, but with greater heterogeneity and a greater presence of large particles in the test carried out with the maximum roller aperture. As the aperture was

Table 10. Results of the chipping tests.

Fruit tree pruning	Average power output (kW)	Testing time (s)	Consumed energy (kWh)	Chipped weight (kg)	Bulk density (kg/m ³)	Efficiency (kWh/kg)
Blade chipper	1.778	366	0.181	10.750	198.8	0.017
Roller mill (minimum aperture)	0.724	770	0.155	5.308	233.47	0.029
Roller mill (maximum aperture)	0.623	642	0.121	5.110	175.33	0.024

so large, on numerous occasions, the prunings passed through the rollers without the rollers exerting any action against the branches.

Table 10 shows the results of the chipping tests.

The most relevant result is that the highest efficiency is achieved with the roller mill (minimum aperture) with a value of 0.029 kWh/kg, almost double the efficiency obtained by the blade chipper.

Figure 3 shows the instantaneous power values over the elapsed time of each test. It can be seen that the values of the two roller mill tests are practically the same, while the blade chipper values are much higher.

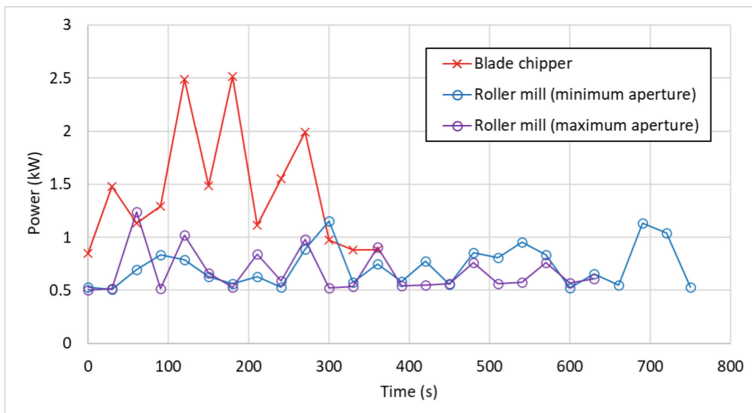


Fig. 3. Instantaneous power values from chipping tests.

It is difficult to compare the chipping results of such small electric chippers as they are not found in the literature. On the other hand, there are studies on the chipping of small Power-Take-Off driven chippers [22].

4 Conclusions

Fruit tree prunings can be used as biofuel in medium-sized domestic heating equipment. The ash percentage is somewhat high for use in smaller equipment. However, they have optimal thermal properties, like HHV.

In order to be used in domestic thermal equipment, it is necessary to undergo a series of pre-treatments, mainly drying and chipping.

Given the results obtained in tests of drying, from the point of view of heat utilization, the drying could be a solution for further use as a biofuel.

The most efficient chipping test of those carried out in this study was achieved with the blade chipper. The chipping of prunings improves logistics and adds value to the waste to be used as biofuel.

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References

1. Fruit Today Euromagazine. <https://fruittoday.com/extremadura-sigue-impulsando-la-mejora-vegetal-para-mantener-su-liderazgo-en-ciruela-y-cereza/>. Accessed 12 Jan 2022
2. Suali, E., Sarbatly, R.: Conversion of microalgae to biofuel. *Renew. Sustain. Energy Rev.* **16**, 4316–4342 (2012)
3. García-Maraver, A., Popov, V., Zamorano, M.: A review of European standards for pellet quality. *Renew. Energy* **36**, 3537–3540 (2011)
4. Miranda, M.T., Montero, I., Sepúlveda, F.J., Arranz, J.I., Rojas, C.V., Nogales, S.: A review of pellets from different sources. *Materials* **8**(4), 1413–1427 (2015)
5. Roy, S., et al.: Removing harvest residues from hardwood stands affects tree growth, wood density and stem wood nutrient concentration in European beech (*Fagus sylvatica*) and oak (*Quercus* spp.). *Forest Ecosyst.* **9**, 100014 (2022)
6. Rijo, B., Soares Dias, A.P., Ramos, M., Ameixa, M.: Valorization of forest waste biomass by catalyzed pyrolysis. *Energy* **243**, 122766 (2022)
7. Biomass from agricultural pruning and plantation removals. A feasible practice promoted by the UP_Running Project. CIRCE, CERTH (2019)
8. UNE-EN ISO 18134-2:2017: Solid Biofuels. Determination of Moisture Content. Oven Dry Method. Part 2: Total Moisture. Simplified Method. AENOR, Madrid (2017)
9. UNE-EN ISO 18123:2016. Solid Biofuels. Determination of the Content of Volatile Matter. AENOR, Madrid (2016)
10. UNE-EN ISO 18122:2016. Solid Biofuels. Determination of Ash Content. AENOR, Madrid (2016)
11. UNE-EN ISO 18125:2018. Solid Biofuels. Determination of Calorific Value. AENOR, Madrid (2018)
12. UNE-EN ISO 17828:2016. Solid Biofuels. Determination of Bulk Density. AENOR, Madrid (2016)
13. UNE-EN ISO 16948:2015. Solid Biofuels. Determination of Total Content of Carbon, Hydrogen and Nitrogen. AENOR, Madrid (2015)
14. UNE-EN ISO 16994:2017. Solid Biofuels. Determination of Content of Sulfur and Chlorine. AENOR, Madrid (2017)
15. UNE-EN ISO 16967:2015. Solid Biofuels. Determination of Major Elements - Al, Ca, Fe, Mg, P, K, Si, Na and Ti. AENOR, Madrid (2015)
16. Senadeera, W., Bhandari, B.R., Young, G., Wijesinghe, B.: Influence of shapes o selected vegetable materials on drying kinetics during fluidized bed drying. *J. Food Eng.* **58**, 277–283 (2003)
17. López, A., Iguaz, A., Esnoz, A., Virseda, P.: Thin-layer drying behaviour of vegetable wastes from wholesale market. *Drying Technol.* **18**, 995–1007 (2000)
18. Chupakhin, E., et al.: Methods of increasing miscanthus biomass yield for biofuel production. *Energies* **14**, 8368 (2021)
19. Larnaudie, V., Ferrari, M.D., Lareo, C.: Switchgrass as an alternative biomass for ethanol production in a biorefinery: perspectives on technology, economics and environmental sustainability. *Renew. Sustain. Energy Rev.* **156**, 112115 (2022)
20. Montero, I.: Modelado y Construcción de un Secadero Solar Híbrido Para Residuos Biomásicos. Ph.D. thesis, University of Extremadura, Badajoz, Spain (2005)
21. Mujumdar, A.S.: *Drying Technology in Agriculture and Food Sciences*. Science Publishers Inc., Enfield (2000)
22. Kuptz, D., Hastmann, H.: Evaluation of fuel quality, throughput rate and energy consumption during non-industrial wood chip production with three PTO driven chippers. *Croatian J. Forest Eng.* **43**, 109–122 (2022)



Design Sustainable Products in a Circular Economy Context

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Abstract. Consumers are increasingly accepting of items based on a sustainable design or project; as a result, corporations should consider these several characteristics while developing new products.

In this work we intend to analyse the environmental impact of the production and manufacturing from the conception and design stage, up to the disassembly of the products, using software and simulation routines dedicated to the assessment of the environmental impact of the materials, production, distribution and end-of-life strategies using the SOLIDWORKS Sustainability.

The work is divided into several parts: definition of sustainability in the development of products; legal proceeding; environmental impact analysis studies throughout the life cycle assessment (LCA) of a product; case study of a plastic cup. The environmental impact of materials will be studied from the stage of obtaining raw materials, through transport, production, use and disposal (or restart as a new product) supported by the concept of circular economy.

Finally, simulations of production process variables will be carried out to minimize the environmental impact, reduce waste and energy, which will have multiple beneficial implications for the industry.

Keywords: Design for disassembly · Topology optimization · Simulations · LCA · Circular economy

1 Introduction

Consumers are becoming increasingly concerned about the environmental impact of the products they purchase, and companies are being held liable for these consequences.

On the other side, it's clear that developing and producing “environmentally friendly” products must be a global concern. As well as achieving sustainability, for the entire economic and productive systems (and environment at a global scale). In addition, the

three principles of circular economy should be used: waste and pollution should be eliminated; circulations of products and materials (at their highest value); regeneration of nature/ biological cycle [1].

1.1 A Sustainable Design

The concept of “Sustainable Design” has been brought into the spotlight to the point where it must be considered when developing new goods and concepts. However, it is often difficult to truly describe this concept, as there are numerous elements that must be considered. Using SOLIDWORKS Sustainability, a software capable of doing product lifetime analysis, it’s possible to estimate the weight of a part or assembly on the environment, in the project phase before its production.

Having the ability to access insights on the environmental impact and studying multiple alternatives in this early phase is extremely interesting. It allows companies to make informed decisions about the chosen materials or what productive process to adopt before the production starts.

Accordingly, to a 2018 study by Nielsen, named *Sustainable Shoppers*, approximately three quarters of the youngsters, referred to as *Millennials* and *Gen Z*, would be willing to pay more for items and services if they addressed these environmental concerns [2].

1.2 Technologies and Topology Analysis

Although we all have a sense for what “sustainability” is, it can be quite difficult to define it. The World Commission on Environment and Development, known as the Brundtland Commission, created one of the best-known and often used definitions: - *Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs* [3].

The major issue is that the entire production and economics systems have evolved in such a way that their methods of operation degrade the environment and tend to continue to grow indefinitely.

We can see sustainability as the balance between the natural world and human construction. This interaction has three components: environmental, social and economic. Sustainability is represented as the intersection of the three domains, reflecting the hierarchy between them, where: a *healthy* economy, depends on a *healthy* society, and both depend on a *healthy* environment [4].

It’s worth noting that the notion of “sustainable design” refers to the intelligent application of sustainability concepts to engineering and design in general. There are a series of topics associated to sustainable design that should be taken into consideration for a future analysis of the environmental impact of the products. Such as:

- Design for disassembly is a design approach that enables the easy recycling of parts, components, and materials from products at the end of their life [5].
- Product stewardship is based on the principle that all those involved in the lifecycle of a product should share responsibility for reducing its environmental impact. Therefore, setting up an effective waste-reduction system and practice [6].

- Cradle to cradle, because product lifecycles should be viewed as cradle to cradle, rather than cradle to grave, to be sustainable. All the elements of a product that has reached the end of its useful life should be designed to go somewhere where it can serve as the input to another system [7].
- Green marketing, is the practice of promoting environmentally sustainable products. Now, some of these products have led to the emergence of very strict guidelines issued by various committees on how to be a “green/sustainable” product.

In order to make changes to products and their productive processes, it is much easier to do so early in the process, before the production phase. It is usually needed some software, namely Life Cycle Assessment (LCA) software and according to ISO 14040/14044 a method for calculating the environmental impact of a product over its entire life cycle, since the acquisition of raw materials, production, distribution, utilization, end of life and recycling (see Fig. 1).



Fig. 1. Life cycle of a product

This type of software relies on a database with all the material, production processes, means of transportation and their impacts, as well as the end of life of the products information. The accuracy of these analysis depends greatly on this database, that should be constantly updated. The interpretation of the results of these studies must be done in a clear, quantifiable, and verifiable way, according to standard ISO 14044, which makes sure the results are analyzed and conclusions are met. In the end, there should be recommendations reported in a clear and transparent manner. These results must also be easily presented, in a way that is understandable, complete and consistent with the actual LCA results.

In a study conducted a few years ago, in 65 companies that employed LCA software, the most applied tools were: 58% used GaBi (Sphera), 31% utilized SimaPro (Pré Consultants) and 11% employed TEAM (Ecobilan) [8]. It is also important to take into consideration that a product design should also consider an easy disassembly process. Therefore, less effort and energy are spent when it comes to recycling or reusing it. This

was not accounted in this study, but it should be taken into account in the development stage of the product.

2 Methodology and Results

2.1 Main Methodologic Steps

In this research, the component to be designed was developed from several simulations supported by the SOLIDWORKS Sustainability, which is a LCA software, totally integrated with SOLIDWORKS CAD. It provides a result for the environmental impact in real time, as the products are developed and designed by the designers. Its use is very simple, with an intuitive interface, and its results are derived from the inputs given by the designer and the geometry of the product.

It uses a GaBi database developed by PE-International, in Stuttgart, Germany.

The Solidworks Sustainability should be used as a dashboard for the environmental impact of the designs, giving immediate feedback on the choices and changes made by the designers. Although it can be seen as a simple LCA software, it uses a very comprehensive database that runs a series of complex analysis in the background, and it's the same database used by some more "advanced" LCA software in the market.

There are 4 metrics used by SOLIDWORKS Sustainability to measure the environmental impact of the products: non-renewable lifecycle energy demand, carbon footprint, air acidification and water eutrophication (see Fig. 2), [9–11].

In this case study, it will be analyzed the environmental impact of the life cycle of two scenarios:

- 1st it will be used a PET polymer cup material, with 460 ml in volume. The differences in several aspects of its lifecycle will be analyzed such as the material, place of production, place of utilization, mean of transport and end of life parameters.
- 2nd it will be used a PS polymer cup material, that is a versatile synthetic organic polymer.

It should be noted that by material it is defined a substance (in solid state but other condensed phases can be included) to be used for certain applications. Nowadays there are a lot of materials available for multiple applications. The main classes of materials are metals, semiconductors, ceramics and polymers. New and advanced materials that are being developed and include nanomaterials, biomaterials and energy materials. The complex combination of these produce the performance of a material in a specific application. A wide variety of features impacts the material performance, from the constituent chemical elements, it's microstructure, and macroscopic features to processing. Together with the laws of thermodynamics and kinetics materials scientists aim to understand and improve materials. The polymer PET is a relatively high-density polyester made from an amorphous or semi-crystalline thermoplastic. It has transparency but low mechanical properties such as tensile strength as well as substantially low slip features [12, 13].

These four parameters are precisely the ones that must be defined in a LCA study in SOLIDWORKS Sustainability. The material can be defined in the CAD design itself

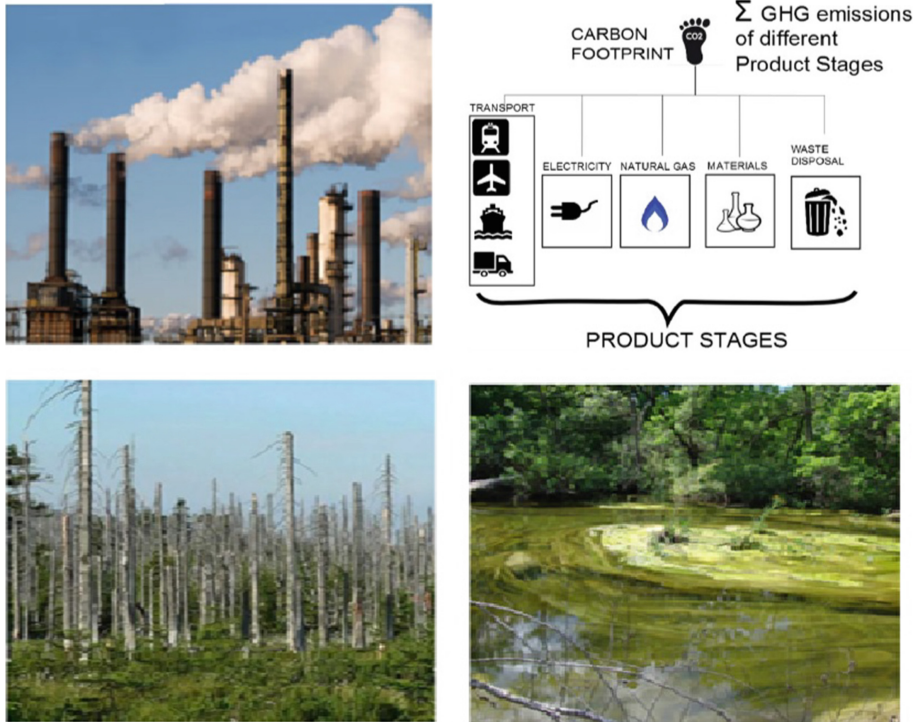


Fig. 2. Four metrics used by SOLIDWORKS Sustainability

and then read by the study; the place of manufacturing and the process parameters must also be defined such as Injection Molded, Extrusion, Custom or None.

- The attribution of the place of use of the product is also important, mostly because of the distance the products must travel between manufacturing and usage, but also because it defines the end-of-life parameters of the product. For example, in some places of the world most of the products are recycled but in other areas they get incinerated.
- The mean of transportation must also be defined as varied transports have different impacts such as a train, trucks, boats and planes.
- The last parameter is the end of life, which is defined by the place of usage, but its parameters can be customized by the designer.

Next two scenarios are simulated related to the material typology of a product are presented: PET and PS polymer cup (see Figs. 3 and 4) with some results from the simulations performed.

For the initial study, the cup is made of PET plastic, produced in Asia by injection mold, used in Europe and the transport is done by sea, with the end-of-life parameters suggested by the software.

With this first set of parameters, we can conclude that the values for each metric are:



Fig. 3. PET cup



Fig. 4. PS cup

- Carbon footprint: 0.091 kg CO₂e
- Energy consumed: 1.6 MJ
- Air acidification: 5.8e-4 kg SO₂e
- Water eutrophication: 3.9e-5 kg PO₄e

In the next step, we will change the parameters and see the impact of the changes. The changes that will be done are:

- Modifying the material to one that has smaller environmental impact (for example, PS). SOLIDWORKS Sustainability is extremely helpful in this regard, as it suggests alternative materials that meet a set of criteria set by the designer. The substance might alternatively be changed to a paper-like material, but the goal is to keep the manufacturing procedure the same. This modification, using PS, allows a decrease in density of ~24% and a reduction in thermal conductivity of ~3.8%.
- Bringing the manufacturing location closer to the usage location, hence reducing the distance between the two. The mode of transport shifts as well, from boat to truck.
- Altering the geometry while retaining the cup's internal volume by employing a wider but shorter cup.

2.2 Results and Discussion

After material change, the carbon footprint was reduced by 32% in the carbon footprint, 28% in the energy consumption, 24% in the air acidification and 20% in water eutrophication.

Bringing the manufacturing location closer to the usage location, we get a decrease of 19% in the carbon footprint, 0% in the energy consumption, 64% in the air acidification and 36% in water eutrophication.

It's interesting to verify that there is a decrease in the carbon footprint, even though the material and manufacturing method were not altered. This is related to the change of the "internal" database parameters that "know" that the manufacturing methods in Europe are different than the ones used in Asia.

Another interesting point is that the transportation weight in the carbon footprint metric increased, even if the distance decreased from 16093 km to 1931 km; this is due to the change of the mean of transportation, from boat to truck, which shows that it is not that linear that the decrease in distance really decreases every aspect of the environmental impact. Changing the geometry showed an overall decrease of ~4% in all metrics.

Discussing these general results, it can be stated that all changes have an environmental impact on cup production: changing the material from PET to PS had an overall impact of 20–30% in all metrics; having a local supplier also helps decreasing the environmental impact, but the means of transport used should also be taken into account; although the change in geometry did not have a significant impact, it may be a very important point overall, because it allows all logistics to be modified, items to be packaged in a different way, possibly lowering overall package volume, allowing new packaging solutions, and so on.

Finally, it should be noted that PS easily mixes with polyolefins but is a contaminant and cannot be processed with them. On the other hand, PET, which also cannot be processed together with other materials. To be reused in the same application, it goes through a very expensive process with high energy consumption, it goes through an intermediate extrusion and crystallization process. Therefore, in the comparison, this issue may have been considered or not, associated with PS there is drying and associated with PET there is crystallization, imagining that we have the manufacturing company at the door of two petrochemical companies, one produces PET and the other produces PS, the costs processing of PET will undoubtedly be superior.

It is also important to mention that in the recycling of materials, it is already necessary to consider, not only the physical recycling, more conventional, which is nothing more than the change of shape, but also the chemical recycling, which is transforming polymers into monomers and these again in polymers, to achieve a truly circular economy.

3 Conclusions

As a conclusion, the initial results were compared with the final ones, and a decrease in all metrics were obtained: 1) 49% decrease in the carbon footprint, from 0.091 to 0.047 kg CO₂e; 2) 32% decrease in the energy consumption, from 1.6 to 1.1 MJ; 3) 75% decrease in air acidification, from 5.8e−4 to 1.5e−4 kg SO₂e; 4) 54% decrease in water eutrophication, from 3.9e−5 to 1.8e−5 kg PO₄e.

This represents a great improvement in the environmental impact, although "in real life", most of the times is not that simple to accomplish all this changes to a project/product. Also, the financial impact was not taken into account, yet in a real-life situation, this is quite essential.

This software relies on the input of parameters for many metrics, however getting the exact values for each parameter might be difficult in many circumstances. There are more complicated LCA studies, including ones that use real, measurable data, but they are much more expensive and time demanding.

This type of research is becoming more relevant as the market becomes more involved in environmental issues and concerns, yet somehow the circular economy concept's application should be a component in reducing these negative factors. In a general sense, we can conclude that there are several key parameters to be given due regard as the development of products happen: 1) The material used, which must meet the project requirements, such as physical rigidity or intended aesthetics, while maintaining an acceptable cost and minimal impacts; 2) Getting a local provider and reducing the amount of material needed for the product, maximizing the percentage of material that comes from a recycled source and using material that can also be recycled or reused. Changing the geometry decreasing the amount of material needed and even helping with the logistics part of the entire process; 3) In companies, the option to manufacture in an environmentally friendly manner has the potential to provide a financial benefit, as the choice of the best material or production technique can also impact this aspect.

References

1. Ellen MacArthur Foundation: What is a circular economy? <https://ellenmacarthurfoundation.org/topics/circular-economy-introduction/>. Accessed 13 Nov 2021
2. NielsenIQ Group: Report Sustainable Shoppers. <https://nielseniq.com/global/en/insights/>. Accessed 3 Jan 2022
3. Simon, D.: Our common future: report of the world commission on environment and development (book review). *Third World Plann. Rev.* **9**(3), 285 (1987)
4. Purvis, B., Mao, Y., Robinson, D., Three pillars of sustainability: in search of conceptual origins (2019)
5. Pensar Group: Afterlife: A Guide to Design for Disassembly. <https://pensar.com/design-for-disassembly/>. Accessed 10 Dec 2021
6. Environment and Climate Change Canada. <https://www.canada.ca/en/environment-climate-change/services/managing-reducing-waste/html>. Accessed 04 Jan 2022
7. Ideiacircular/Cradle to Cradle - C2C. <https://www.ideiacircular.com/o-que-e-cradle-to-cradle/>. Accessed 04 Jan 2022
8. Cooper, J.S., Fava, J.: Life cycle assessment practitioner survey: summary of results. *J. Industr. Ecol.* (2006)
9. Lewis, H., Gertsakis, J., Grant, T., Morelli, N., Sweatman, A.: *Design + Environment: A Global Guide to Designing Greener Goods*, Greenleaf Publications (2001)
10. Fantossi, F., Bartocci P.: Carbon Footprint as a Tool to Limit Greenhouse Gas Emissions; Chapter book Greenhouse Gases/Project: Life Cycle Assessment (2016). <https://doi.org/10.5772/62281>
11. Ma, F., Wang, W., Sun, Q., Liu, F., Li, X.: Ecological pressure of carbon footprint in passenger transport: spatio-temporal changes and regional disparities. *Sustainability* **10**, 317 (2018). <https://doi.org/10.3390/su10020317>
12. Materials science – Wikipedia. https://en.wikipedia.org/wiki/Materials_science#Emerging_technologies. Accessed 25 Nov 2021
13. Pradhan, S., Rajamani, S., Agrawal, G., Dash, M., Samal, S.: 7 - NMR, FT-IR and Raman Characterization of Biomaterials, Chapter book, pp. 147–173 (2017). <https://doi.org/10.1016/B978-0-08-100737-2.00007-8>



Designing a Sustainability Plan for La Salve Brewery

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Abstract. In this paper the design of a Sustainability Plan for the Salve brewery is modelled. To support transition for decarbonization of the company ensuring a triple zero production (energy, waste, and transport), the critical points during the production process have been identified from a SWOT analysis. Using the CLEWs tools (through the OSeMOSYS software), five scenarios are designed and evaluated according to the company energetic needs. Both historical set of real consumption data of the company, as well as the growth expectations raised by the owners have served as the basis for the work. To simplify the decision making to the company, both investment and total associated costs as well as the corresponding CO₂ emissions has been estimated in the period 2023–2030. As main results, an energetic scenario including the use of bagasse waste, the implementation of photovoltaic solar energy and avoiding the fossil fuels, allows to achieve the planned objective with an economic contribution assumable by the company. In addition, several potential business niches associated with the circular economy have been identified.

Keywords: Sustainable energetic transition · CLEWs · Circular economy · Brewery

1 Introduction

La Salve is a traditional historical brewery, created in 1886 in Bilbao (Euskadi Region, Spain). The brewery, maintaining the philosophy from its origins, is committed to generating local value and wealth in the environment. For this reason, it is currently a company that is constantly searching for innovation and sustainable development. In this paper the design of a Sustainability Plan for the company to reach the expectations of a complete production's decarbonization (Triple Zero Philosophy Beer) across a sustainable transition is presented.

To identify the main sources of unsustainability, a SWOT matrix, in terms of Lifetime Analysis (LCA), has been performed [1]. The extended LCA indicators are considered as the adequate unbiased estimators to evaluate the economic, energetic, and environmental

sustainability of any product/process/initiative. Following a “cradle to cradle” scheme, the raw materials, the production beer process, the packaging, the associated waste, and the distribution process as well as their environmental impact contribution are clarified.

One of the processes identified as a threat is the energy consumption associated with both production and transport for distribution. However, it can also be considered as an opportunity, if an environmentally friendly energetic system is designed. Because La Salve is mostly a local company, distribution constitutes a small percentage of the overall energetic needs being the most consuming both electric and heating components. The heating demand is linked to the production, fermentation and washing processes.

Given the economic implications and logistics that have arisen, the task of modeling suitable scenarios towards *Zero Energy Production* is not easy, particularly for a highly productive and constantly developing company like La Salve. The company’s expectations are to have enough information to make informed decisions having knowledge of the effects of any initiative in the medium to long term previously to its implementation.

These concerns are common to the entire business fabric. In the current nexus frameworks for sustainable development, tools are being developed to fulfill the explained request. Among them, OSeMOSYS [2, 3], an open-source tool that allows predictive modeling of economic optimization of any energy scenario. OSeMOSYS can be freely applied according to the user’s needs and allows to evaluate a set of scenarios of its MoManI interface [4].

This work is focused on the feasibility study and economic optimization of a series of possible energy transition initiatives that allow decarbonizing (*Triple Zero*) the production processes of the La Salve brewery using the OSeMOSYS tool.

2 La Salve Brewery

The Brewery of La Salve is in Bilbao (42.5° N latitude), with a moderate Atlantic climate. It occupies 628.61 m² in surface. In the subsoil is located a tank of homogenization of wastewater.

Figure 1 shows an outline of the processes associated with the beer production process. The company has provided data on raw materials, process and energies used during the production of beer, as well as modes of transport and distances along the supply chain.

Raw Materials. The raw materials mainly used are malt, hops, yeast, water, and some additives. The company purchases within the nearby markets the malt, which is the main beer component [5]. In addition, the brewery is involved in an innovative project that promotes the local hops production [5]. As for the yeast, up to 80% is reused.

With respect to the water needs, the plant is supplied with water from the network, since the quality is adequate for the beer production [1].

Packaging. The most common packaging are barrels and glass bottles. Currently, the brewery is evaluating various options for reducing the footprint associated with this process, which is undoubtedly one of the most demanding in economic, energetic, and environmental terms [1]. In particular, the barrels with less impact of the market are used [6]. Bottles with 48% recycled glass [7] are being used nowadays.

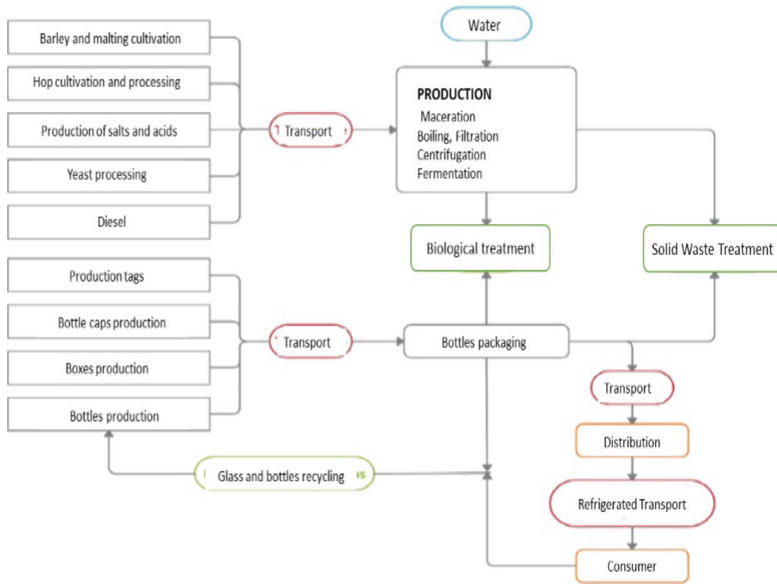


Fig. 1. Beer production scheme in La Salve

Energetic Consumption. The brewery is supplied by the national electricity grid, with a contracted consumption of 70 kW and an average annual consumption of 90 MWh. Concerning the thermal demand, the factory is supplied by 200 kg/h generated by a steam boiler powered by diesel as natural gas is not available in the region.

3 Methodology

The economic viability of different scenarios is evaluated using OSeMOSYS [2, 3] (Open-source Energy Modeling System) and its MoManI interface [4].

The brewery total decarbonization is performed through a linear optimization considering the energetic mix. As results are discussed: i) the new installed energetic capacities per technology; ii) the economic global cost and iii) associated emissions. Several scenarios, attending to the SWOT matrix internally developed by the company [1, 8] are defined and evaluated. The time interval defined for the study goes from 2022 to 2030. Data prior to 2022 are considered for validation. As working hypothesis, following the actual Spanish regulations no taxes associated to the pollutant emissions are included.

4 Evaluation of Scenarios for Sustainable Transition

As explained before, the energy requirements to be met are twofold: electricity and hot water (2095 kl/year). Among the possible initiatives towards sustainability, different scenarios are proposed: those dedicated to the search for biofuels to replace fossil

fuel, the ones obtaining of electricity from renewable energy sources and finally mixed solutions that encompass the problem in a global way. Finally, scenarios focused on full decarbonization will be evaluated. To model the scenarios, all the parameters, including technical and economical, are identified. La Salve power system has been modeled using OSeMOSYS. To validate the model, the available data prior to 2020 have been considered. consequently, the improvement actions will be applied from 2023.

4.1 La Salve's Current Situation: Business as Usual (BAU)

The BAU scenario is defined as a frozen version of the energetic system. The long-term evaluation of BAU allows the evaluation of the non-insertion of new initiatives into the nexus energetic mix. Table 1 shows the overall energetics needs. To adapt the system during the study period, an annual increasing rate of 3% is considered to the electric cost.

Table 1. Current energetic (thermal and electric) La Salve's consumption. Types, demands, and costs. [8, 9]

Electricity		Gasoil		Water	
Contracted power	50 kW	Calorific value	43100 kJ/kg	Consumption	2095 kL/year
Cost increase	3% per year	Consumption	14440 kg/year	Fuel cost	5.4 €/kL
Fuel cost	164.17 €/MWh	Fuel cost	0.8235 €/kg	Boiler	
Emissions	0.18 tCO ₂ /MWh	Emissions	0.0033 tCO ₂ /kg	Capacity	0.056 kg/s

4.2 Evaluation of Sustainable Thermal Scenario (SUSTHE)

To face an agenda towards decarbonization, the challenge is to reduce and/or avoid the use of polluting fuels. In that sense, scenarios based on the replacement of the gasoil used as fuel by La Salve to heat water, with more sustainable ones indeed, exist several options: from green electricity, geothermal, or wood combustion (chips or pellets). Considering the wood combustible solution, exists an oil boiler that can be adapted for wood-pellet burning with the same operational useful lifetime.

In addition, this solution is favored by allowing the reuse of the company's main waste: The bagasse produced during the malt cooking process, which can be pelletized. A dedicated study shows a promising calorific potential [1].

Table 2. Types, demands, and costs of the technologies included in the scenario. [1, 8, 10–12]

	Bagasse	Pellet	Pelletizer		Boiler Adapter
Fuel cost	0	0.0052 €/kg	Capacity	0.28 kg/s	
Calorific value	12131 kJ/kg	1882.8 kJ/kg	Inversion Cost	22,000 €	20,000 €
Disponibility	55360 kg/year	Necessary	Fuel Cost	0.018 €/kg	

A first rough calculation shows that the current production of bagasse will be insufficient to cover the total calorific needs. However, since this type of waste can be pelletized, unmet needs can be covered by standard pellets, from the local production when possible.

Resuming, the proposed scenario will be allowing the replacement of the fossil fuel (BAU) with pellets, both own and nearby purchased. For this, two investments are envisaged: the adaptation of the boiler and, for the reuse of bagasse, a pelletizer machine. The specific database used is included on Table 2.

The SUSTHE scenario has been evaluated using OSeMOSYS modeling tool. As can be seen in Fig. 2 (a), the elimination of gasoil as a fuel in favor of the pellet constitutes the economically optimal solution despite the costs associated with the adaptation of the boiler and the pelletizer.

Figure 2. (b) shows the total costs, including initial investments, the price of fuels (gasoil, the electrical cost of the pelletizer bagasse or external pellets), as well as maintenance. The important initial investment associated to this scenario during the first two years is recovered with the lower price of the pellet respect to gasoil.

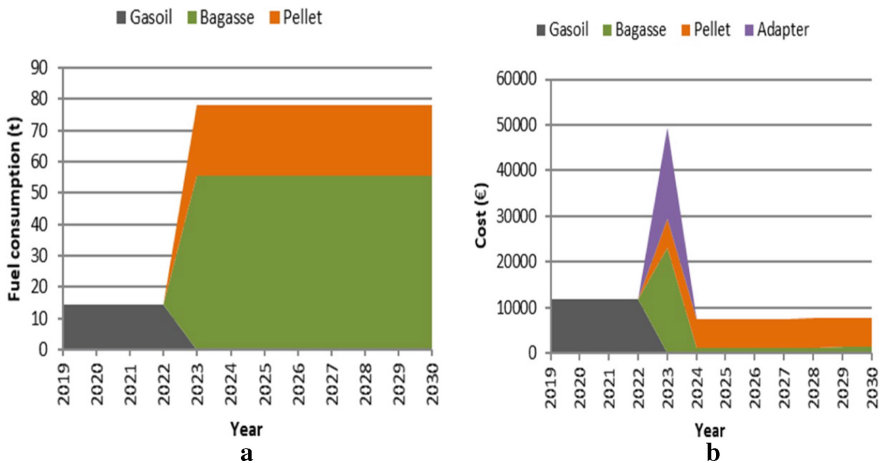


Fig. 2. On the left (a) Annual fuel consumption. On the right (b) Expected total cost along the evaluation period. The slight cost after 2024 in bagasse corresponds with associated electric variable costs of the pelletizer.

As a final remark, the associated CO₂ emissions strongly decreases with respect to the BAU. This is because the pelletized material coming either forest residues or the bagasse residues themselves, have zero emission associated.

4.3 Evaluation of Sustainable Electric Scenarios (SUSELE)

Within the framework of the sustainable transition process, the need to advance in a process of energy independence, the so-called “Zero energy” is imposed. The current configuration of the Spanish electricity system favors the implementation of local electricity production systems grid-connected working in “Net Balance” regime.

In addition, the so-called “after counter” accumulation systems are currently beginning to be popularized. This type of system favors a stable and controlled injection to the electric grid while economically benefiting the producer.

Table 3. Types, demands, and costs of the Solar Photovoltaic and accumulation technologies. [3, 8, 14–16]

	SOLAR (panels)	Batteries (storage)
Maintenance cost	100.72 €/MWh	–
Inversion cost	3284.17 €/MWh disimintion 2% per year	53960–99920 €/MWh
Operational life	12 years	6 years

To study the economic viability of the proposal, a specific scenario has been designed and evaluated using the OSeMOSYS tool. Technically, the simplest solution is the implementation of a photovoltaic solar energy roof-plant, eventually associated to an accumulation system. Moreover, to favor circular economy processes, second-life ion-lithium batteries (coming from electric cars) are proposed as storage system. So, as working hypothesis, to the BAU scenario constrains, the opportunity of including both PV systems and/or storage system is included. The specific database used is included on Table 3.

As shown in Fig. 3, a gradual implementation of PV technology grid connected constitutes the most competitive option at economical level. In fact, because of the modularity of PV installations, the high associated initial investment can also be gradual which facilitates the economic logistics of a small company such as Salve. The proposed installed capacity from 50.2 kWp in 2023 to 74.5 kWp in 3030, being able to satisfy 73% of the total electric demand.

The actual price of the second-life ion-Lithium batteries inhibit its contribution to an optimal electric mix of La Salve. A future price drop [16] would induce a reconsideration of the scenario.

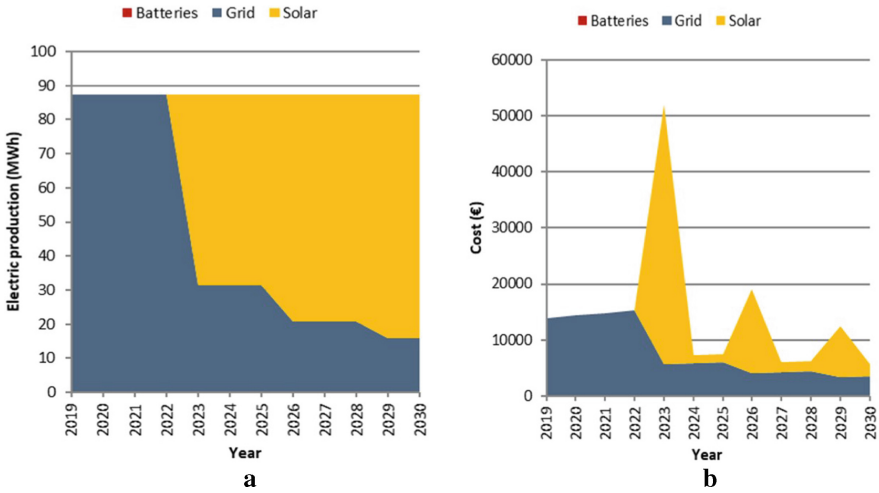


Fig. 3. On the left (a) Yearly electric production by technology. On the right (b) Total cost.

4.4 Global Zero Energy Scenario (ZERO)

In accordance with La Salve’s medium-term expectations, the objective is to achieve a zero global energy system (both thermal and electric). To assess both economic viability and estimated investment, a new scenario has been constructed that combines the above scenarios (BAU, SUSTHE, SUSELE).

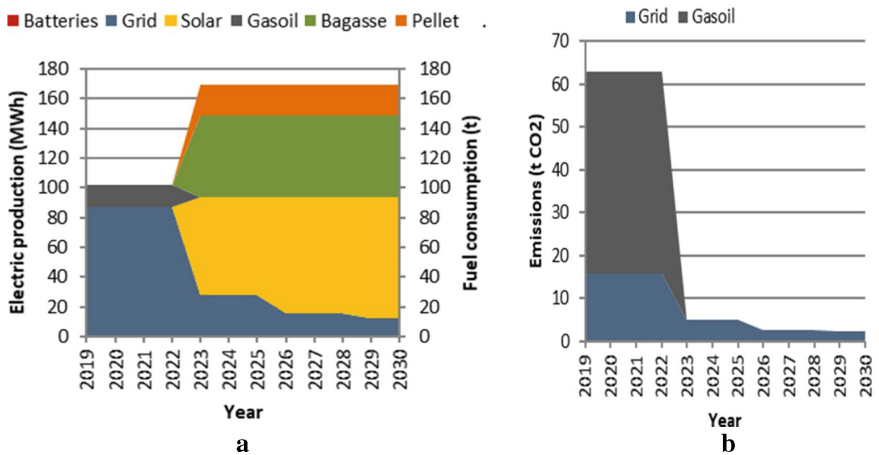


Fig. 4. On the left (a) Annual energetic production by technology. On the right (b) the CO₂ associated emissions.

As a conclusion, while external dependence has sharply decreased, a complete ZERO energy scenario is not economically competitive, being necessary a small dependence on external electrical grid. This is due to both the seasonal instability of the solar resource

and the still high price of accumulation systems. The emissions associated with this scenario (Fig. 4 (b)), show a remarkable decrease, associated with the elimination of fossil fuels in the heating processes, being the remaining emissions legated to the one associated to the electrical network (8% from the BAU scenario).

4.5 Triple ZERO Scenario (ZERO_TRP)

Based on the previous scenarios, a last alternative is proposed, undoubtedly much more ambitious: to convert La Salve’s beer into a product of the so-called *Triple Zero*, that is zero energy, zero waste, zero emissions. It has been seen how the SUSTHE scenario promotes zero waste by using organic waste as biofuel. From the ZERO energy scenario, it has managed to strongly reduce external energetic dependence, even if a small dependence on the electrical grid and its corresponding associated CO₂ emissions remains.

To fulfill the Triple Zero expectative, a new scenario is defined. As new constrain, a linear decrease of the emissions fulfilling the objective of zero emissions for 2030 is applied as work hypothesis. In addition, there is in Spain several electrical companies that offer the possibility of consuming exclusively “green energies” from the network.

This possibility has been contemplated as an added component. This type of energy tariff is around 20% more expensive, although the entry into the market of CO₂ carbon credits can be contemplated. The possibility of including “second life” batteries as energetic source is always open.

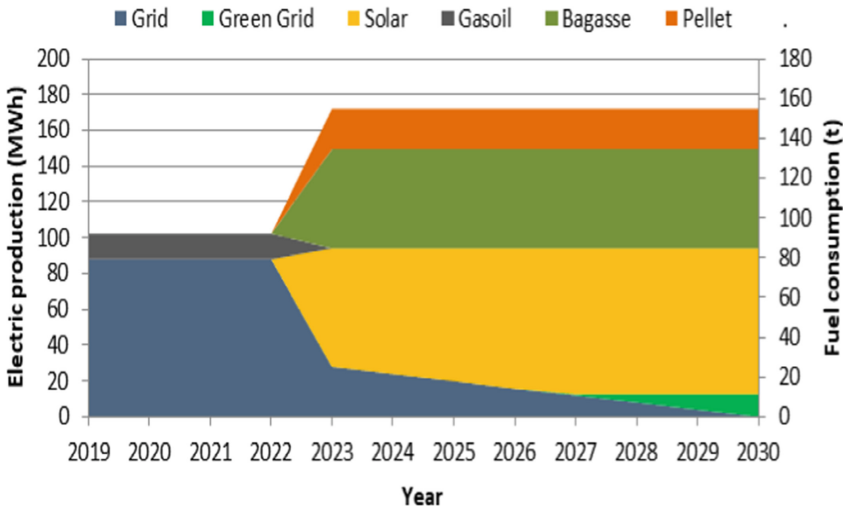


Fig. 5. Annual electric production by technology as well as the thermal fuel consumption.

As main remark, Fig. 5 shows how the “green energy” electric network appears, whereas the current second-life batteries inhibit their use. The implementation costs are like the ZERO scenario.

4.6 Scenarios Comparison for Decision Making

Once the different scenarios have been evaluated, in this section a comparative study is proposed, in both economic and environmental terms to facilitate the company's decision making,

Figure 6 (a) shows the total costs associated with each scenario in the interval under study (2023–2030). New Investment, fuel (either electric or thermal), and maintenance costs are separately evaluated. As can be seen, the ZERO and ZERO_TRP scenarios appear as the most promising. Although they entail heavy initial investments, (close to 100.000 euros) both maintenance and fuel costs make them hardly competitive. The estimated overall saving with respect to BAU is near to 12%.

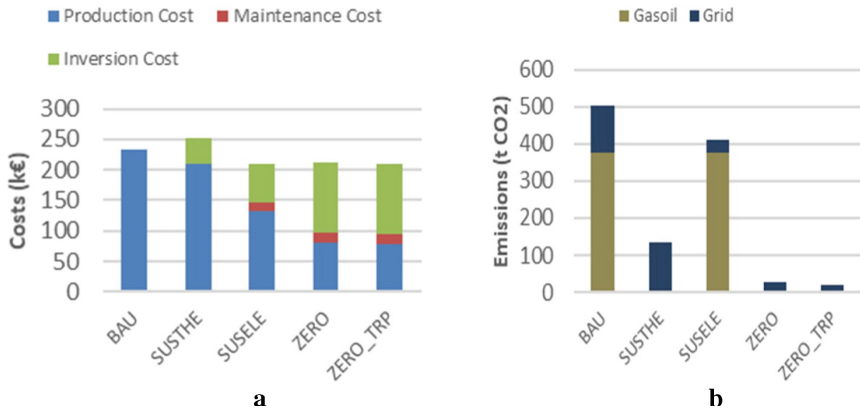


Fig. 6. On the left (a) Total costs, in k€. On the right (b) Total emissions for each scenario between 2023 and 2030.

Finally, in Fig. 6 (b) the emissions associated with the different scenarios are characterized. As can be seen, the SUSTHE scenario appears as the one with the greatest impact facing the decarbonization goal. The ZERO scenario is even stricter since, the implementation of solar panels, decreases the emissions associated to actual electrical grid. As expected, ZERO_TRP scenario, fully achieve expectations of quasi-ZERO energy dependence and ZERO emissions.

5 Conclusions

The design of a roadmap towards the decarbonization of the brewery La Salve is presented. The final objective is an economic feasibility study of different action scenarios that allows the manufacture of *Triple Zero Beer* (energy, waste, emissions). For this, both the detailed data of the company and the corresponding SWOT analysis have been analyzed. From there, the design of a roadmap for sustainable energy transition is identified as a crucial point of the process. Through the OSeMOSYS software, five scenarios are designed and evaluated according to the company energetic needs. To simplify the

decision making to the company, both investment and total associated costs as well as the corresponding CO₂ emissions has been estimated in the period 2023–2030.

As main results, the Triple Zero Beer Scenario (ZERO_TRP) appears as not only possible but the most promising: the zero CO₂ emission can be achieved by 2030, mainly because the use of fossil fuels is avoided.

Although they entail heavy initial investments, (close to 100.000 euros) both maintenance and fuel costs make them hardly competitive. The quasi-ZERO external energetic dependence is accomplished. The 5% of grid-energy production remaining is associated to energetic green sources. The estimated overall saving with respect to the actual working regime is near to 12%.

References

1. Gonzalez del Rey, K.: Diseño de un Plan de Sostenibilidad para la empresacervecer La Salve. Universidad de Santiago de Compostela. Departamento de Física (2021)
2. Introduction to OSeMOSYS—OSeMOSYS 0.0.1 documentation. <https://osemosys.readthedocs.io/en/latest/manual/Introduction.html>. Cited 14 Mar 2022
3. Howells, M., et al.: OSeMOSYS: The Open Source Energy Modeling System. An Introduction to Its Ethos, Structure and Development, vol. 39, pp. 5850–70. Energy Policy (2011)
4. Almulla, Y., et al.: Model Management Infrastructure (MoManI) Training Manual. KTH-dESA, pp. 1–61 (2017)
5. “La Salve”. LA SALVE Bilbao - Cerveza:: Beer :: Garagardoa. Accessed 10 Mar 2022
6. “Enfoqueen la sostenibilidad - KeyKeg.” <https://www.keykeg.com/es/duurzaamheid>. Accessed 31 Mar 2022
7. “Fabricación y venta de envases, botellas y tarros de vidrio | Vidrala.” <https://www.vidrala.com/es/>. Accessed 31 Mar 2022
8. Confidential internal communication with La Salve
9. Poderes Calóricos de algunos Combustibles – RECOPE. Accessed 15 Mar 2022
10. Precio del pellet en España 2021. <https://www.caloryfrio.com/energias-renovables/biomasa/precios-especiales-en-sacos-de-pellets.html>. Accessed 20 Mar 2022
11. Palet de 70 sacos de pellet NATURPELLET · LEROY MERLIN. Accessed 05 Mar 2022
12. China High Efficiency 1-1.5 T/H Wood Pellets Making Machine Ring Die Sawdust Wood Pellet Mill - China Biomass Pellet Machine, Straw Pellet Machine. Accessed 15 Feb 2022
13. García-Gusano, D., Martín-Gamboa, M., Iribarren, D., Dufour, J.: Prospective analysis of life-cycle indicators through endogenous integration into a national power generation model. Resources **5** (2016)
14. Míguez Fariña, A.: Estudio de diferentes escenarios para la transición energética de Galicia mediante el uso de herramientas CLEWs. Universidad de Santiago de Compostela. Departamento de Física (2020)
15. Martínez-Laserna, E., et al.: Battery second life: hype, hope or reality? A critical review of the state of the art. Renew. Sustain. Energy Rev. **93**, 701–718 (2018). Accessed 25 Feb 2022
16. Baterías de segunda vida: Febrero 2021, Informe de la Comunidad Tecnológica de Almacenamiento. PowerPoint Presentation (globalelectricity.org). Accessed 07 Apr 2022



Engagement with the Community and Partnerships for Sustainable Food Production and Consumption in Portuguese Higher Education Institutions

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Abstract. The Sustainable Food Production and Consumption Working Group of the Sustainable Campus Network (RCS) participated, in 2020/21, in a survey of Higher Education Institutions (HEIs) in Portugal. One of the sections of this survey aimed to better understand what is happening in HEIs in terms of the food service sustainability.

Food Production and Consumption is a critical theme for sustainability and has a very high importance within the scope of actions and interventions of HEIs in the society. Training, research, internal practices, and partnerships are easily identified as ways for HEIs to impact society. The work presented here focuses on the results obtained from the survey in terms of existing partnerships and connections within the community.

The survey was answered by 30 HEIs, comprehending Public and Private Universities, Polytechnic Institutes and Non-Integrated Schools. In the set of responses, 24 HEIs (80%) responded positively to the question: “Does the HEI have initiatives for the promotion of sustainable food consumption?”. One of the survey goals’ was to analyse the HEIs “connection to the Community”.

The results show us that there are few references to the relationship regarding the supply chain, namely, on producers and HEI’s. However, references to the traditional HEIs’ partnerships are frequent namely functional research and teaching

partners amongst other scientific areas, active networks, internships, and conferences. A good practice is the brand-new network regarding partnerships focused on the reduction of food waste and evolving academic community.

The results suggest that mainly all the HEIs lack a systemic strategy of building bridges with the community, as a two-way avenue to achieve sustainability.

Keywords: Sustainable food production · Sustainable food consumption · Higher education institutions · Survey · Partnerships

1 Introduction

It is widely recognized that food production and consumption is one of the domains responsible for the largest share of environmental impact, such as Greenhouse Gases (GHG) emissions, water pollution and loss of biodiversity that will increase the global population crisis [1]. Thus, the importance that the food system has in the society, makes it a very critical issue and an opportunity to achieve sustainability, in all of four dimensions, human, social, environment and economic.

The challenge of ensuring the satisfaction of the human needs for food in conditions of sustainability on Earth cannot fail to be a topic at the higher education institutions. Each HEI can inspire its academic community and society in general, with its knowledge and new solutions achieved through training, research, and partnerships. HEIs can undoubtedly evolve themselves because it is their mission to train, research and innovate, but also because they ensure the provision of a wide number of meals to the extent academic community. To the purpose of supplying the food services HEIs establish relationships with the internal and external community but also partnerships. The present study aims to understand if the relationship with the community and partnerships by Portuguese HEIs are sustainability oriented.

In 2020/21, the Sustainable Campus Network (*Rede Campus Sustentável - RCS*), led a survey on Sustainability in the Higher Education in Portugal. The questionnaire was sent to all HEIs inquiring on several aspects regarding the sustainability implementation at each Institution. One of the topics covered was the “Food Production and Consumption”. The questions were designed by the Sustainable Food Production and Consumption Working Group (GT-PCAS) from the RCS. The aim of this survey was, in addition to carry out a first diagnosis of the HEIs, the gathering of initiatives, best practices, instruments used, obstacles encountered and facilitating elements, which may inspire the path towards sustainability specifically concerning the food area [2]. The data presented in this paper specifically refer to the relationship with communities and partnerships, or in other words “linkages to the community”.

2 Literature Review

2.1 Food: The Portuguese Reality

Portugal is a country characterised by a Mediterranean Diet, but it is shifting towards an “occidentalised” diet, where large quantities of animal-based proteins are consumed

[3]. National studies show that the Portuguese are consuming more than three times the amount of meat, seafood and eggs recommended in the National Food Wheel and 33% more dairy, whereas fruits and vegetables are well below the recommended values [4]. Environmental problems such as the Global Warming Potential of the food chain shows that Portugal has the largest contribution value - 1460 kg CO₂ eq./cap.year, whereas the average EU diet shows to contribute with 1070 kg CO₂ eq./cap.year [5]. Food waste is also a severe issue in Portugal, representing 17% of the total food produced for human consumption in the country [6]. Portugal's ecological footprint is almost three times higher than its biocapacity (3.69 gha/cap vs. 1.28 gha/cap) and food consumption has a contribution of 30% to the ecological footprint [7]. In overall, a lot needs to be done to promote national sustainable food consumption practices and HEIs can play a leading role.

Nowadays, Portuguese dietary habits are also one of the main causes of health problems. Since 2017, the Portuguese Nutrition Association (APN) has been developing the "Food Sustainability Program" which aims to increase food literacy, particularly among school-age young people, while raising awareness of the relationship between food and sustainability [8]. But, in general, food literacy is presented as a mainly informative and health-oriented concept. The dissemination of the Mediterranean Diet assisted on providing the support for the raise of the awareness on healthy and more sustainable food consumption patterns [8]. The importance of the use of the Mediterranean Diet for the menu planning in school meals, is also recognised in The Guidelines on School Menus and Canteens [9].

2.2 HEIs and Food Chain Sustainability

It is well known the contribution of food to "good" health. Less frequently looked at is the relationship between food choices and the sustainability in all its dimensions. This happens even though research studies have been showing that this association should not be neglected. The large environmental impacts of the food chain, relies strongly on the industrialised agriculture. Some aspects contributing to the environmental burden are the intensive farming industry with the use of antibiotics, abuse of chemicals and agricultural traditional practices that lead to soil erosion, intensive production of fish and cattle with high methane and other emissions, food distribution based on long circuits, disconnection to local ecological cycles as the seasonality of food and high levels of waste. Simultaneously, the market is led by powerful economic groups that don't internalise the socio-ecological externalities and the distribution of income is often unfair.

The challenge to promote the transformation towards more sustainable practices in the agri-food chain system, requires action by the whole society and its institutions. It is proposed by The Eat-Lancet Commission's report "Food in the Anthropocene" [10] specific measures for the public sector, including schools and universities:

- Government leads the way and promotes what is meant to be "right type of food".
- Empowering schools agents (professors, staff and students) to develop a curricula that can lead to societal and cultural change relationship with food.

HEIs have been addressing issues of sustainability for some decades. Several HEIs sustainable development initiatives, related at the 14th European Roundtable on Sustainable Production and Consumption (ERSCP) & 6th Environmental Management for Sustainable Universities (EMSU) [11], have brought to light some issues on this topic. One of the suggested initiatives were collaboration with other universities and stakeholders, such as the public, governments, non-governmental organisations (NGOs) and businesses, to seek collaboration, engagement, and outreach [11].

HEIs have the means to lead a path to establish a sustainable food chain system. This can be done by cooperating among university in a multidisciplinary approach, creating partnerships in various areas of knowledge and induce a strong relationship with the community. Such actions may constitute the basis to provide the means to change the agri-food system towards a more sustainable path. HEIs can, for instance, suggest policies and models, indicators, new solutions, innovations, and platforms. HEIs can lead by example because are also responsible for feeding millions of people daily. The food service provision also results in a lot of food and packaging waste. Some authors mention that HEIs may act as “sustainability laboratories” and became leaderships to the urgent need of changes [12].

2.3 The HEIs Role and the Importance for Partnerships

Universities, industry, and policy makers can strive together to incentivize these systemic processes, through shared value and common purpose to ensure the persistence of human and planetary health [13]. Some institutions are already taking the lead. There are different HEIs’ action and roles concerning the strategy to networking and the engaging of the community, as an essential key factor. There are a quite number of examples worldwide.

A recent attempt to link environmental impact and food nutrient quality was conducted by a larger research project with the participation of various university departments in Sweden [14].

In United States, according to the work of Ringling & Marquart [13] concerning the creation of a program for Sustainable Food Systems to develop diets that nurture human health required multiple disciplinary actors. The University of Minnesota is well-positioned to play a key role in developing models and frameworks supporting. This integrative, systematic process can improve the efficacy of nutrition research by intimately engaging across the supply chain, thus effectively translating research into practical application [13].

2.4 Experiences About Sustainable Practices of Food Provisions in Schools

In this new paradigm, it is necessary to rethink how to involve the new partners and new actors from the food chain system. Some examples integrating the network are the producers/farmers, the retailers, the distributors, the marketing, the final consumers, the food waste management agents from the HEIs’ canteens and existing bars. The published experiences of new chains mainly refer to school canteens from non-higher education institutions. The published experiences [15–17] analysed the supply to school canteens and concluded that the main point of attention has been the acquisition of

healthy foods, by considering their nutritional value. Delgado [18] reports the pilot experience of supplying local organic food to the canteens of an elementary schools in the Municipality of Torres Vedras and identifies the problem of insufficient supply of products due to lack of availability of land to produce local and organic food. The project reveals the importance of cooperation between schools and municipal departments and between these and the local actors.

This experience follows the example of the project Urbact_BioCanteens in the French city of Mouans Sartoux. The three city school canteens (about 1,400 meals a day) are supplied with 100% organic products, most of which are produced locally. In 2012, were produced 15 tons that covered 50% of the supply and in 2015 it amounted to 85% of the needs. In 2016, these players guaranteed 100% of the vegetables and fruit products consumed in school canteens [19]. Similar examples can be found in public school's canteens in Portugal [20].

In Portugal, the HEIs and Research Centers establish partnerships and collaborate with each other essentially for research projects and publications [21]. Partnerships with the community are less frequently reported, due to that it is important to know how the HEIs are facing this challenge, what are the new experiences, new practices, new relationships with the internal and external community and new partnerships are being established and conducted.

3 Methodology

The survey carried out to all Portuguese HEIs, aimed to better understand what is happening in HEIs in the food sector, to list good and inspiring practices and facilitating actors to implement them. The survey was organized in complementary types of initiatives, namely: i) Education, ii) Research, iii) Management, iv) Partnership and v) Others. The present study is focused just on the answers integrated in the “partnership” thematic. The survey questions were therefore designed to allow open answers describing initiatives, with their own examples, as it is transcribed in the Table 1.

Table 1. Questions from the Survey on Sustainability in Higher Education in Portugal 2020, section “Food Production and Consumption” related to Partnership & Community engagement.

<p>Question: <i>Does the HEI promote initiatives to promote sustainable food consumption?</i></p> <p>Answers: a) No</p> <p style="padding-left: 40px;">b) <i>Yes, through the relation with the community (social actions for the community, inside and outside the campus)</i></p> <p><i>The HEIs were asked to mention the main initiatives developed, the most relevant initiative, the main results, and the facilitating institutions that were involved in initiatives to promote sustainable food consumption.</i></p> <p><i>Finally, the HEIs were asked to specify the main obstacles founded in promoting sustainable food consumption.</i></p>

First, the results were clustered by a review analysis of the answers that in general were endogenous and unique actions to each HEI. The clusters were organised by related thematic and sub-thematic areas and divided in 2 categories: i) External and ii) Internal community and partnerships engagement.

It was considered as “external community and partnerships” all the actors and agents involved in the food system, namely, production and sustainable food consumption, from: local producers, local government, social and non-governmental organizations, education institutions and research project funding agencies. A similar definition was applied to the “internal community and partnerships”, in this case, inter and intra-campus research between organizational units, social welfare and other entities that provide services that plays an important role in promoting networks that design and implement different actions.

All answers were classified in the respective theme and sub-theme and then, counting the total number of responses per theme, whenever possible. There is a subjective component on this step because classification of statements into sub-themes was based on content analysis, with semi-quantitative accounting, so the numerical values should only be read as indicative values. The confidentiality was guaranteed by coding, although some of the HEI reference their name in the answers. The websites and links provided in the answers weren't considered in the transcriptions.

4 Results

The survey was answered by 30 HEIs, Public and Private Universities, Polytechnic Institutes and non-integrated Schools. In the set of responses, 24 HEIs (80%) responded positively to “do you promote initiatives to promote sustainable food consumption?”. Each of 24 HEI indicated the type in which it developed the initiatives, and the “Partnership & Community engagement” obtained around 68% of affirmative answers.

In the partnership type of initiatives, 48 were considered external and 43 were considered internal partnerships and community engagement.

4.1 External Community and Partnerships

Table 2 shows the 48 listed statements where the repeated ones were only counted in the total number of statements, organized by sub-themes. The results show that external partnerships occur between health, governmental, social, and environmental entities. enterprises also appear with commercial projects and products. There are new partnerships dealing with food waste and bio-waste management. Mainly this links happens due to students' internships places. The local food production is one of the less frequencies' answers.

Table 2. 48 listed statements about external partnerships for sustainable food consumption organised by sub-thematic and respective percentage.

Sub-thematic	Statements	%
Health, research, local and national government entities, and organizations supporting children and the elderly	Health entities: DGS General Health Directorate; ARS Regional Health Administration; Local Health Units <ul style="list-style-type: none"> • Municipalities: CMLeiria, CM Funchal and CM Porto and another not described. Parish Council of Paranhos. Municipal companies: Novo Verde, Porto Ambiente, Lipor • DGAV - General Directorate of Food and Veterinary Medicine, • Secretary of State for Food and Agri-Food Research • National Institute of Agricultural and Veterinary Research • Public Education Establishment and Private Kindergarten Association, • Elderly homes 	37,5
Business Entities	<ul style="list-style-type: none"> • Food industry, distribution and retail companies: Nestlé, Continente, El Corte Inglés; Nigel, GoNatural, Sustainmeals; Calé, Receituariuim, Algaplus, Nautilus, Emanha, Frubaça; Cup; APCER; 2Go Out Consulting • Entities hosting interns, campaign development, food product innovation and quality management - implementation of the HACCP system 	35,4
Associations: Public and Private	Non-Governmental Organizations: Doca Pescas; Lemon People Cooperative; ReFood; Caregivers Portugal; FAO Portugal; AGAVI; Dariacordar Association; Food Bank Against Hunger; Blue Flag Association of Europe – ABAE	18,8
Local producers	Organic local producers and short supply chains	4,2
Project Financing Agencies	FCT, H2020, ADI, PRIMA, ERA-Net ARIMNet2	4,1

4.2 Internal Community and Partnerships

Table 3 shows the list of the 43 statements where the repeated ones were only counted in the total number of statements, organized by sub-themes. The results shows that internal partnerships occur mainly through research projects, with Social Action Services (SAS)

and between different academic curricular courses. The less frequent answers are those that evolve students, or HEI community. There are activities for the academic community, but few are organized with the academic community.

Table 3. List of 43 statements about internal partnerships for sustainable food consumption organised by sub-thematic and respective percentage.

Sub-thematic	Statements	%
Research projects, Inter-institutional, national, and international cooperation	Network of Higher Education Institutions to Safeguard the Mediterranean Diet; College F3 – Food, Farming & Forestry; AGRO Network - Interdisciplinary Thematic Network for Agro-Food and Forestry; 5 a Day Program - Integrates the Alianza Internacional de Asociaciones Y Movimientos “5 al Día” (AIAM5); Healthy Campus; National Observatory of Organic Production; Colab4Food; COTHN; CCPAM; MAFDR; GROW CROPS; INOVIMIL; MobFood; Zero Waste Project; Right Dose Project; city loops	39,5
Between SAS-social action services, with schools and faculties, with research centers, with nutrition courses	Partnership with schools, collaborative networks; interdisciplinary research institute, with schools and faculties, library; students, nursing professionals; 3rd year students of the Tourism and Hotel Management course Application for the Food Excellence Seal (DGS) and implementation of operational measures Development of initiatives to encourage the reduction of food waste, calling for adequate consumption, monitoring of waste and promoting measures to optimize processes and resources. Awareness campaigns through messages in the canteen, in the media and on social networks	25,6
Interdisciplinary	Degree, schools and faculties of Nutrition Sciences, other scientific areas and courses, other schools and faculties, schools of health, tourism, agriculture, science. Involvement with curricular units for the development of food icons	20,9

(continued)

Table 3. (continued)

Sub-thematic	Statements	%
Project for the community	Intra-campus: workshops, practical training, community empowerment; Promotion of the habit of eating breakfast; Seal of Excellence for Sustainable Food, Food waste, organic waste, and recycling campaigns Intra and extra campus: events: the community is invited to participate, attend, or also promote their products; Health and Wellness Office and nutrition consultation	9,3
Student projects	Old Fashioned Fruit; donation of clean leftover food	4,7

5 Conclusions

The results show that:

- There were slightly more external partnerships and community engagement type of initiatives than internal, regarding the number.
- there are few references to the relationships within the supply chain, namely to producers, but no reference to traditional relationships nor to new partnerships. It appears that the canteens food suppliers are not considered to be potential partnerships with influence towards more sustainability practices.
- The main and traditional HEI's partnerships are research and teaching partners among other scientific areas, networks, internships, and scientific events. A brand-new network of partnerships is focused on the reduction and/or management of food waste.
- The internal academic community actions that evolve all, are scarce and are top-down oriented.
- There were few initiatives with the students' as stakeholders
- We also assume the need to connect local production with the food supply school canteens needs is not yet explored.

We are led to conclude that the adoption of a new food cycle chains that could catalyse sustainability food production and consumption action in HEIs appears to be incipient.

This study is embraced by the GT_PCAS to be further developed in ongoing and future actions. These results should be seen as a first analysis, as we know that it is still possible to “widen” (there are more HEIs working on the topic) and “deepen” (the HEIs that responded did not map everything they do).

Despite the recognized relevance, the legislation, and the official national strategies to promote sustainable food production and consumption, this topic is not a daily reality

practice, at HEIs. This restriction is highlighted by some HEIs, who claim that implementing sustainable food production and consumption is a difficult challenge due to the complexity of the actual and installed food system (production and distribution), food costs, social culture, habits, traditions, available resources and the limitations to HEIs actions posed by public procurement rules and laws. It is crucial to pursue the goals, through action-research to achieve cooperative solutions of the main causes of HEIs food sustainability production and consumption claim.

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References

1. Azzurra, A., Massimiliano, A., Angela, M.: Measuring sustainable food consumption: a case study on organic food. *Sustain. Product. Consum.* **17**, 95–107 (2019)
2. Soares, A., Neto, B., Farinha, C., Avelar, D., Alves, E., Santos, J.: Análise das respostas obtidas ao inquérito, sobre sustentabilidade no Ensino Superior em Portugal, promovido pela Rede Campus Sustentável, com foco na sustentabilidade da produção e do consumo alimentar, 3rd Conferencia Campus Sustentável (CCS2021) (2021)
3. Bento, A.: Comer bem é o melhor remédio (P. Editora Ed. 1st edn). Porto Editora (2017)
4. Lopes, C.T., et al.: Inquérito Alimentar Nacional e de Atividade Física, IAN-AF 2015–2016: Relatório de resultados (2017)
5. Sandström, V., Valin, H., Krisztin, T., Havlík, P., Herrero, M., Kastner, T.: The role of trade in the greenhouse gas footprints of EU diets. *Glob. Food Sec.* **19**, 48–55 (2018)
6. Baptista, P., Campos, I.S.G., Pires, I.V.: Do Campo ao Garfo, Desperdício Alimentar em Portugal. Edição de CESTRAS. Lisboa (2012)
7. Galli, A., et al.: Sustainable food transition in Portugal: assessing the footprint of dietary choices and gaps in national and local food policies. *Sci. Total Environ.* **749**, 141307 (2020)
8. Santos, G.D.S.T.: Alimentação Sustentável nas escolas públicas portuguesas: educação e compras públicas [Dissertação de mestrado, Iscte - Instituto Universitário de Lisboa]. Repositório Iscte (2020). <http://hdl.handle.net/10071/21541>
9. Lima, M.R.: Orientações para Ementas e Refeitórios Escolares, Ministério da Educação-Direção Geral da Educação (2018). <http://www.dge.mec.pt/sites/default/files/Esauade/oere.pdf>
10. Willett, W., Rockström, J., Loken, B., et al.: Food in the anthropocene: the EAT–Lancet, commission on healthy diets from sustainable food systems. *Lancet* **393**, 447–492 (2019)
11. Lozano, R., Lukman, R., Lozano, F.J., Huisingh, D., Zilahy, G.: Jumping sustainability meme; SD transfer from society to universities. In: The Knowledge Collaboration and Learning for Sustainable Innovation ERSCP-EMSU Conference, Delft, The Netherlands, 25–29 October 2010 (2010)
12. Schmidt, L., Nave, J.G., Guerra, J.: Educação Ambiental: balanço e perspetivas para uma agenda mais sustentável, Lisboa: ICS (2010)
13. Ringling, K.M., Marquart, L.F.: Intersection of diet, health, and environment: land grant universities' role in creating platforms for sustainable food systems. *Front. Sustain. Food Syst.* **4**, 70 (2020). <https://doi.org/10.3389/fsufs.2020.00070>
14. Strid, A., Hallström, E., Sonesson, U., Sjons, J., Winkvist, A., Bianchi, M.: Sustainability indicators for foods benefiting climate and health. *Sustainability* **13**, 3621 (2021)

15. Sonnino, R.: Quality food, public procurement, and sustainable development: the school meal revolution in Rome. *Environ Plan A* **41**(2), 425–440 (2009). <https://doi.org/10.1068/a40112>
16. Wahlen, S., Heiskanen, E., Aalto, K.: Endorsing sustainable food consumption: prospects from public catering. *J. Consum. Policy* **35**(1), 7–21 (2012). <https://doi.org/10.1007/s10603-011-9183-4>
17. Palacios-Argüello, L., Gonzalez-Feliu, J., Gondran, N., Badeig, F.: Assessing the economic and environmental impacts of urban food systems for public school canteens: case study of Great Lyon region. *Eur. Transp. Res. Rev.* **10**(2), 1–20 (2018). <https://doi.org/10.1186/s12544-018-0306-8>
18. Delgado, C.: Produzir alimentos biológicos e locais para abastecer as cantinas escolares: opções políticas de acesso à terra. *Publ. Policy Portuguese Journal* **6**(2), 132–153 (2021)
19. Rodrigo, J., Rioufol, V.: Supporting access to land for farmers in Europe. **162** (2017). https://agrimadre.net/wp-content/uploads/2018/04/Access_to_Land_Supporting_access_to_land_for_farmers.pdf
20. Bizarro, S., Ferreiro, M.D.F.: Sustainable public procurement in Portugal: the case of two public school canteens. *Region. Sci. Policy Pract.* (2021)
21. Farinha, C., Caeiro, S., Azeiteiro, U.: Universities speak up regarding the implementation of sustainable development challenges: the case of Portugal. *Int. J. Sustain. High. Educ.* **21**(3), 465–506 (2020). <https://doi.org/10.1108/IJSHE-08-20190250>



Thermodynamic and Kinetic Analyses of Corn Crop Residue

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Abstract. Corn crop is one of the most important crops worldwide. However, the management of the residue generated is not efficient enough, which diminishes the competitiveness of this crop. An interesting option for the valorisation of these waste is their thermal use. For the development of the present study, different types of residue from corn crop were selected, depending on the proportion of corn cob waste and stalk, which were collected from local crops in the southwest of Spain. The objective of this research was to investigate the thermal characteristics and thermochemical process kinetics of the corn crop residue. Non-isothermal thermogravimetry technique was used at different heating rates of 10, 20 30 and 40 °C/min under oxidative atmosphere. Regarding the heating rate on combustion of corn crop residue it can be observed that ignition and final temperature increased with increase in heating rate whereas the temperature at which the maximum weight loss rate is observed remains more or less constant, with no significant effect due to the heating rate. Concerning the activation energy, three isoconversional methods have been used, Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Starink, resulting that in general the activation energy decreases as the conversion takes place, indicating the presence of an exothermic reaction.

Keywords: *Zea mays* · Thermogravimetric analysis · Kinetic study

1 Introduction

At present, corn is one of the world's main crops, together with other cereals such as wheat and rice, and is an essential source of food for human beings. If we consider the situation of corn crops in Spain, according to FAO, it is one of the ten most important crops in this country [1].

After harvesting the corn grain, a waste called stover is produced, which consists of a mixture of different parts of the corn plant, i.e., the stalk, the corn cob waste from the dekernelled cob and the leaves, both from the stalk and those that envelop the cob itself. Currently, this waste is left on the ground, being mechanically shredded to be mixed

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with the soil after harvesting. Occasionally, this residue is used to produce bales for use in biomass power plants or for livestock purposes. In the past, in Spain, corn stover was burnt in the fields, with the risk and environmental impact that this entailed. Fortunately, this practice is in disuse [1].

In order to obtain a competitive improvement in corn crops, at the same time as achieving a reduction in environmental impact, within the framework of a circular economy, it is interesting to study the recovery of the waste generated, with one of the possible applications of this waste being its energy use.

For the study of thermal processes and their possible energy use, thermogravimetric analysis (TG) is a basic tool, as it allows the suitability of corn residue as biofuels to be evaluated, as well as determining the thermal process with the best performance. For this purpose, thermogravimetric analysis will be carried out at different heating rates, in order to reach significant conclusions about the combustion process. On the other hand, the kinetic reactions of the process will be modelled as a tool to obtain a complete description of the thermal combustion process.

2 Materials and Methods

The following is a description of the different types of residue studied, as well as the different tests used in this work.

2.1 Sample Collection and Preparation

For the development of the present study, different types of waste from corn were selected, which were collected from local crops in the southwest of Spain.

Currently, harvesters separate the cob from the stalk. Hence, it would be interesting to compare both types of waste separately, i.e., for one thing, the cob waste with the leaves covering the cob and, for another thing, the corn stalk with the leaves. It is also interesting to compare the characteristics of the cob residue with and without leaves to assess the effect of the leaves on the thermal properties of this residue, as separation would be an easy process to implement. The last waste would be the stover that is finally left on the soil.

The following table identifies the different types of waste covered by this study (as a continuation of the work carried out in Miranda *et al.* [1]) and their main characteristics (Table 1):

The samples were ground in a hammer mill (CIP Line SG40, Italy), using a 5 mm sieve at the exit of the machine. Afterwards, in order to obtain an optimum granulometry, the samples were ground in a ball mill (Retsch MM 301, Germany).

2.2 TG Analysis

The thermogravimetric analysis (TG) was carried out by using a thermobalance (NETZSCH STA 449F5 Jupiter, Germany), located in the Cork, Wood and Charcoal Institute belonging to CICYTEX. Different samples from each residue were selected, with variable weights from 18 to 45 mg in an aluminum crucible (Al₂O₃), undergoing temperatures between 30 to 900 °C, at heating rates of 10, 20, 30 and 40 °C/min in air atmosphere

Table 1. Samples studied in the present work.

Name	Waste	Leaves	Soil contact
Ma1	Corn cob	No	No
Ma2	Corn cob	Yes	No
Ma3	Stalk	Yes	No
Ma4	Corn cob + Stalk	Yes	Yes

(80/20) with a gas flow of 50 mL/min. The protective gas was argon (20 mL/min). To conduct properly the thermogravimetric analysis the Difference Thermogravimetric curve (DTG) has been calculated, corresponding to the first derivative of the DT curve. All the samples were done in triplicate in order to assure a suitable reproducibility of results.

In order to determine the different temperature events, the tangent method [2, 3], has been selected. Concerning the temperature at which combustion or burning ended, it was considered when the residual mass was 1% of the original mass [3, 4]. Thus, the ignition temperature, T_i (corresponding to the starting temperature of the thermal process according to the tangent method), the burnout temperature, T_f , and peak temperature, T_p , (the temperature at which the maximum weight loss rate was observed) were determined.

2.3 Kinetic Analysis

The conversion of biomass from solid state to volatile state during combustion is an heterogeneous reaction, and the rate of reaction can be written as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where α is the rate of conversion within sample, t is the time and k the reaction rate constant. According to Arrhenius, the reaction rate constant k is represented by the following equation:

$$k = Ae^{-\left(\frac{E}{RT}\right)} \quad (2)$$

where A is the pre-exponential factor (min^{-1}), E is the activation energy (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K). The conversion factor, α , is represented by Eq. (3):

$$\alpha = \left(\frac{\alpha_0 - \alpha_t}{\alpha_0 - \alpha_f} \right) \quad (3)$$

where α_0 is initial weight of biomass, α_t is weight of biomass at a particular time and α_f is mass of biomass at the end of the combustion. According to the previous equations the rate of reaction can be written as follows:

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E}{RT}\right)} f(\alpha) \quad (4)$$

Considering Arrhenius equation, $G(\alpha)$ integral form of conversion, and for non-isothermal conditions in a linear heating rate, β (K/min), Eq. (5) can be obtained:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} e^{-\left(\frac{E}{RT}\right)} dT \quad (5)$$

In this study, to determine the activation energy using TG data, at different heating rates for combustion of corn residue, three isoconversional methods have been used. These methods, Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Starink, are the three commonly used integral methods [5].

Flynn-Wall-Ozawa (FWO) Method. The Flynn-Wall-Ozawa method is used to calculate activation energy using Doyle's approximation [6]. The FWO method [7, 8] is represented by the following equation:

$$\ln(\beta) = \ln\left(\frac{AE}{RG(\alpha)}\right) - 5.331 - 1.052\left(\frac{E}{RT}\right) \quad (6)$$

According to this method, activation energy is estimated from the slope of equation obtained from the plot of $\ln(\beta)$ and $1/T$ at different heating rates. At each conversion, activation energy is calculated from the slope $-1.052 E/R$.

Kissinger-Akahira-Sunose (KAS) Method. The KAS method [9, 10] is represented by the following equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{EG(\alpha)}\right) - \frac{E}{RT} \quad (7)$$

Here, activation energy is calculated with the aid of plot between $\ln(\beta/T^2)$ and $1/T$ at different heating rates. At each conversion, activation energy is calculated from the slope $-E/R$.

Starink Method. The Starink method [11] is represented by the following equation:

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = C_s - 1.0008 \frac{E}{RT} \quad (8)$$

where C_s is a constant. Here, $\ln(\beta/T^{1.92})$ and $1/T$ is plotted to obtain a set of lines at different conversions. At each conversion, activation energy is calculated from the slope $-1.0008 E/R$.

3 Results and Discussion

3.1 Thermal Behaviour

The combustion profiles of the different corn crop waste at four heating rates are shown in Fig. 1.

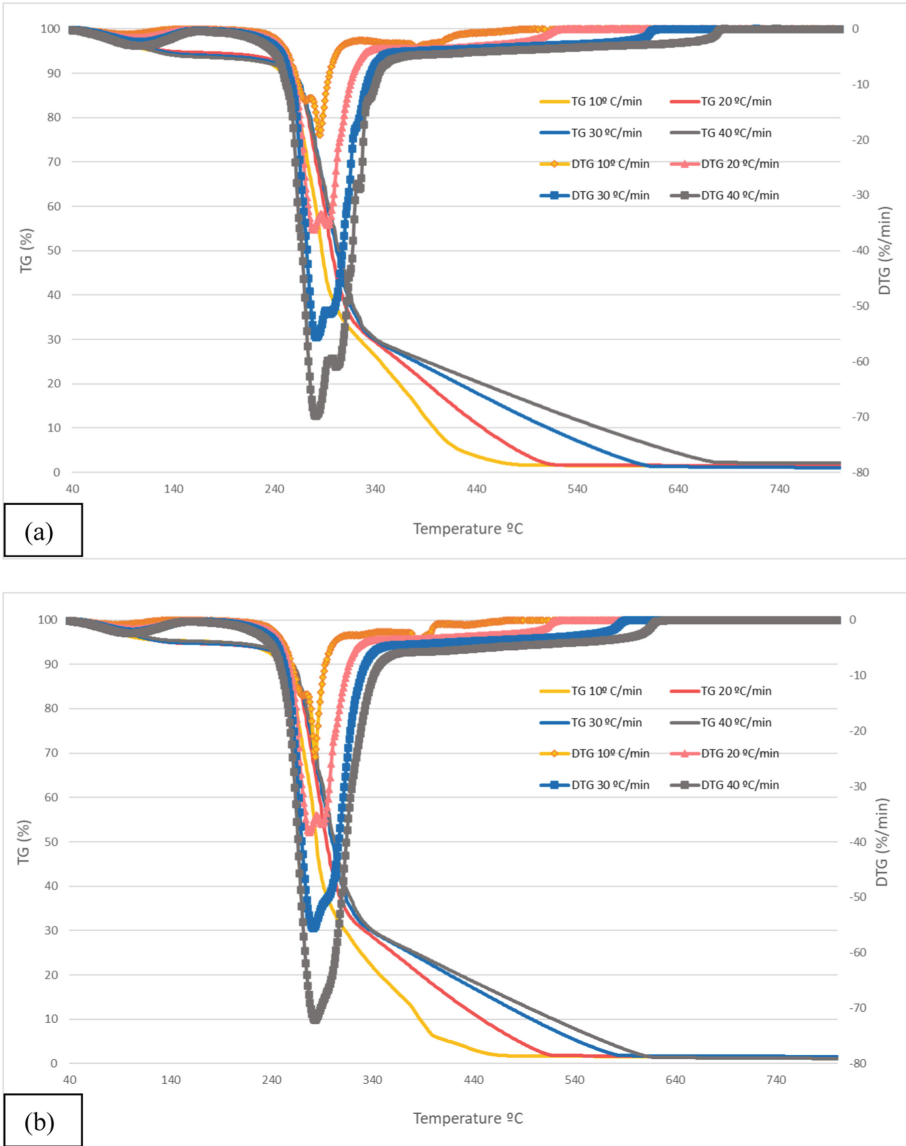


Fig. 1. (a) TG and DTG – Ma1, (b) TG and DTG – Ma2, (c) TG and DTG – Ma3 and (d) TG and DTG – Ma4.

The thermal degradation takes place in three stages. The first stage was related to moisture loss, from room temperature to the temperature at which 5% weight loss took place [12]. At higher temperatures, a faster stage started with the combustion of volatile compounds, observing a temperature peak due to the thermal decomposition of cellulose and hemicellulose, up to the final temperature of this stage, where a change in the slope of the TG curve took place. The third stage corresponded to lignin decomposition and

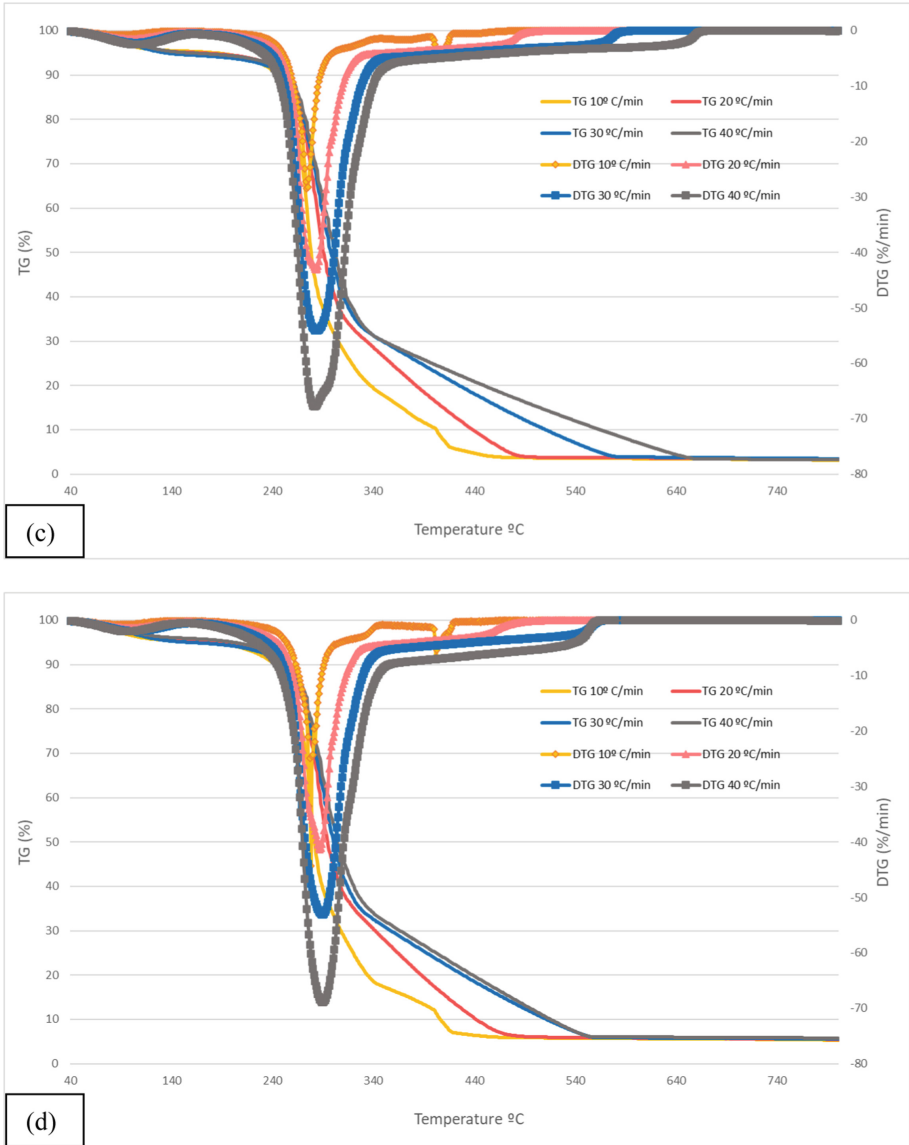


Fig. 1. (continued)

char combustion, finishing at the burning temperature. Lastly, a final stage took place up to 900 °C, the temperature at which the test finished.

In the case of samples Ma1, Ma2 and Ma3, it can be seen that T_i and T_f increased with increase in heating rate whereas T_p remains more or less constant with no significant effect due to the heating rate. In the case of sample Ma4 it can be observed that T_i , T_p and T_f increased with increasing heating rate; this may be due to the fact that the

higher impurity content means that the heat is not transmitted well into the sample, so that a temperature gradient is produced between the outside and the inside of the biomass, thus, the higher the heating rates is the greater this gradient is, and the sample needs higher temperatures for its decomposition. The increase of thermal degradation processes towards higher temperatures due to the increase of heating rate has been reported in multiple bibliographies [13, 14].

3.2 Kinetic Analysis

The kinetic parameters were calculated by Eqs. **Error! Reference source not found.**), **Error! Reference source not found.**) and **Error! Reference source not found.**) from FWO, KAS and Starink method, respectively. Activation energy and correlation coefficient at different conversions are shown in Table 2, Table 3 and Table 4, for different methods.

Activation energy is the minimum amount of energy required to initiate a reaction. The average activation energy obtained from FWO, KAS and Starink methods, for Ma1 residue, was found to be 226.01, 227.98 and 228.19 kJ/mol, respectively. In the case of Ma2 residue, the results obtained were 212.50, 213.82 and 214.04, respectively. Finally, for Ma3 residue the results were 205.24, 206.24 and 206.47, whereas from Ma4 residue were 232.00, 234.40 and 234.06, respectively. Comparing the results of the different types of waste, it can be observed that Ma4 residue needs higher activation energy, which may be due to the higher content of impurities in the residue, as it has undergone degradation during the time spent in the soil. Regarding the average activation energy is very similar among the rest of the waste, with better characteristics being observed in the case of the stalk. On the other hand, in the case of the corncob waste, the leaves enveloping the corncob improve the characteristics, so it does not make sense to eliminate these leaves. Compared to other studies, Sattar *et al.* [15] observed an activation energy of 205.76 kJ/mol for corn cob waste, and Arranz *et. al* [16] obtained a value of 205.64 kJ/mol for rice husk, values very similar to those obtained in the present study.

The values of the average correlation coefficient, R^2 , is higher than 0.98 for all the samples and in all three methods, which means a good fit with experimental data and a relatively accurate estimation.

Table 2. FWO method.

Conversion (α)	Ma1			Ma2		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -43.761x + 78.877$	0.9660	345.85	$y = -46.515x + 83.825$	0.9945	367.61
0.2	$y = -38.33x + 68.113$	0.9969	302.92	$y = -40.349x + 71.688$	0.9876	318.88
0.3	$y = -35.715x + 62.541$	0.9980	282.26	$y = -35.588x + 62.427$	0.9980	281.26
0.4	$y = -28.869x + 49.731$	0.9937	228.15	$y = -26.69x + 46.026$	0.9923	210.93
0.5	$y = -25.003x + 42.368$	0.9979	197.60	$y = -22.543x + 38.188$	0.9972	178.16
0.6	$y = -29.553x + 49.127$	0.9837	233.56	$y = -24.034x + 39.873$	0.9973	189.94
0.7	$y = -20.375x + 31.409$	0.9966	161.02	$y = -12.234x + 18.547$	0.9968	96.68
0.8	$y = -7.178x + 9.433$	0.9688	56.73	$y = -7.158x + 9.532$	0.9952	56.57
<i>Average</i>		<i>0.9877</i>	<i>226.01</i>		<i>0.9949</i>	<i>212.50</i>
Conversion (α)	Ma3			Ma4		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -67.441x + 122.602$	0.9980	532.99	$y = -83.171x + 150.458$	0.9868	657.30
0.2	$y = -38.887x + 69.435$	0.9952	307.33	$y = -47.137x + 83.915$	0.9969	372.53
0.3	$y = -28.595x + 50.262$	0.9981	225.99	$y = -28.059x + 48.989$	0.9853	221.75
0.4	$y = -20.646x + 35.608$	0.9989	163.17	$y = -24.235x + 41.759$	0.9947	191.53
0.5	$y = -19.184x + 32.584$	0.9977	151.61	$y = -19.498x + 32.941$	0.9979	154.09
0.6	$y = -17.87x + 29.565$	0.9980	141.23	$y = -17.461x + 28.7$	0.9947	138.00
0.7	$y = -9.454x + 14.246$	0.9897	74.72	$y = -9.279x + 13.952$	0.9842	73.33
0.8	$y = -5.679x + 7.445$	0.9837	44.88	$y = -6.003x + 8.07$	0.9812	47.44
<i>Average</i>		<i>0.9949</i>	<i>205.24</i>		<i>0.9902</i>	<i>232.00</i>

Table 3. KAS method.

Conversion (α)	Ma1			Ma2		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -42.668x + 64.27$	0.9644	354.75	$y = -45.42x + 69.215$	0.9942	377.62
0.2	$y = -37.223x + 53.481$	0.9967	309.47	$y = -39.241x + 57.053$	0.9869	326.25
0.3	$y = -34.594x + 47.881$	0.9978	287.61	$y = -34.468x + 47.771$	0.9978	286.57
0.4	$y = -27.734x + 35.049$	0.9941	230.58	$y = -25.558x + 31.349$	0.9926	212.49
0.5	$y = -23.853x + 27.659$	0.9977	198.31	$y = -21.396x + 23.483$	0.9969	177.88
0.6	$y = -28.375x + 34.37$	0.9823	235.91	$y = -22.86x + 25.123$	0.9970	190.06
0.7	$y = -19.121x + 16.526$	0.9961	158.97	$y = -10.991x + 3.681$	0.9962	91.38
0.8	$y = -5.804x + -5.635$	0.9517	48.26	$y = -5.81x + -5.495$	0.9925	48.31
<i>Average</i>		<i>0.9851</i>	<i>227.98</i>		<i>0.9943</i>	<i>213.82</i>
Conversion (α)	Ma3			Ma4		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -66.351x + 108$	0.9980	551.64	$y = -82.074x + 135.843$	0.9865	682.36
0.2	$y = -37.784x + 54.81$	0.9949	314.14	$y = -46.028x + 69.278$	0.9967	382.68
0.3	$y = -27.482x + 35.62$	0.9980	228.49	$y = -26.941x + 34.336$	0.9841	223.99
0.4	$y = -19.522x + 20.943$	0.9987	162.31	$y = -23.105x + 27.086$	0.9940	192.10
0.5	$y = -18.046x + 17.896$	0.9974	150.03	$y = -18.354x + 18.242$	0.9976	152.59
0.6	$y = -16.705x + 14.829$	0.9977	138.89	$y = -16.291x + 13.957$	0.9940	135.45
0.7	$y = -8.225x + -0.597$	0.9866	68.38	$y = -8.052x + -0.887$	0.9794	66.94
0.8	$y = -4.34x + -7.571$	0.9706	36.08	$y = -4.699x + -6.893$	0.9702	39.07
<i>Average</i>		<i>0.9927</i>	<i>206.24</i>		<i>0.9878</i>	<i>234.40</i>

Table 4. Starink method.

Conversion (α)	Ma1			Ma2		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -42.712x + 64.854$	0.9644	354.83	$y = -45.464x + 69.799$	0.9943	377.68
0.2	$y = -37.267x + 54.066$	0.9967	309.59	$y = -39.285x + 57.639$	0.9869	326.36
0.3	$y = -34.638x + 48.468$	0.9978	287.75	$y = -34.513x + 48.358$	0.9978	286.71
0.4	$y = -27.78x + 35.636$	0.9941	230.77	$y = -25.603x + 31.936$	0.9926	212.69
0.5	$y = -23.899x + 28.248$	0.9977	198.54	$y = -21.442x + 24.072$	0.9969	178.12
0.6	$y = -28.422x + 34.961$	0.9823	236.11	$y = -22.907x + 25.713$	0.9970	190.30
0.7	$y = -19.171x + 17.122$	0.9961	159.26	$y = -11.04x + 4.276$	0.9962	91.72
0.8	$y = -5.859x + -5.032$	0.9526	48.67	$y = -5.864x + -4.894$	0.9926	48.72
<i>Average</i>		0.9852	228.19		0.9943	214.04
Conversion (α)	Ma3			Ma4		
	Equation	R ²	E (kJ/mol)	Equation	R ²	E (kJ/mol)
0.1	$y = -66.394x + 108.585$	0.9980	551.56	$y = -82.117x + 136.428$	0.9865	682.18
0.2	$y = -37.828x + 55.395$	0.9949	314.25	$y = -46.072x + 69.864$	0.9967	382.74
0.3	$y = -27.527x + 36.205$	0.9980	228.67	$y = -26.985x + 34.922$	0.9841	224.18
0.4	$y = -19.567x + 21.53$	0.9987	162.55	$y = -23.151x + 27.673$	0.9940	192.32
0.5	$y = -18.091x + 18.483$	0.9974	150.29	$y = -18.4x + 18.83$	0.9977	152.85
0.6	$y = -16.752x + 15.418$	0.9977	139.16	$y = -16.338x + 14.547$	0.9940	135.73
0.7	$y = -8.274x + -0.003$	0.9867	68.74	$y = -8.101x + -0.294$	0.9797	67.30
0.8	$y = -4.394x + -6.97$	0.9713	36.50	$y = -4.751x + -6.295$	0.9708	39.47
<i>Average</i>		0.9928	206.47		0.9879	234.60

4 Conclusions

The results confirmed that corn crop waste can be used as biofuel due to their suitable thermal characteristics. However, it is concluded from the results obtained that the contact of the residue with the soil worsens its thermal characteristics and impairs the optimal development of combustion.

This effect can be observed by comparing the activation energy of the process, with worse results being obtained for the waste that has remained on the ground. As for the other three types of residue, the activation energy is higher for the case of the corncob waste without leaves, followed by the corncob waste with the leaves enveloping the corn cob, with the lowest activation energy being observed in the case of the stalk.

On the other hand, as for the kinetic models, the mean values obtained for each method were similar, with a similar pattern throughout the conversion process, so they are considered valid methods for the determination of the thermal properties of corn crop waste.

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References

1. Miranda, M.T., García-Mateos, R., Arranz, J.I., Sepúlveda, F.J., Romero, P., Botet-Jiménez, A.: Selective use of corn crop residues: energy viability. *Appl. Sci.* **11**(7), 3284 (2021)
2. Chen, Q., et al.: Investigation of heat of biomass pyrolysis and secondary reactions by simultaneous thermogravimetry and differential scanning calorimetry. *Fuel* **134**, 467–476 (2014)
3. Mureddu, M., Dessì, F., Orsini, A., Ferrara, F., Pettinau, A.: Air - and oxygen-blown characterization of coal and biomass by thermogravimetric analysis. *Fuel* **212**, 626–637 (2018)
4. Lu, J.J., Chen, W.H.: Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by thermogravimetric analysis. *Appl. Energy* **160**, 49–57 (2015)
5. Singh, R.K., Patil, T., Sawarkar, A.N.: Pyrolysis of garlic husk biomass: physico-chemical characterization, thermodynamic and kinetic analyses. *Bioresour. Technol. Rep.* **12**(September), 100558 (2020)
6. Doyle, C.D.: Series approximations to the equation of thermogravimetric data [13]. *Nature* **207**(4994) (1965)
7. Ozawa, T.: A new method of analyzing thermogravimetric data. *Bull. Chem. Soc. Jpn.* **38**(11), 1881–1886 (1965)
8. Joseph, L.A.W., Flynn, H.: A quick, direct method for the determination of activation energy from thermogravimetric data. *J. Polym. Sci. Part B Polym. Lett.* **4**, 323–328 (1966)
9. Kissinger, H.E.: Reaction kinetics in differential thermal analysis. *Anal. Chem.* **29**(11) (1957)
10. Sunose, T., Akahira, T.: Method of determining activation deterioration constant of electrical insulating materials. *Res. Rep. Chiba Inst. Technol. (Sci. Technol.)* **16**, 22–31 (1971)
11. Starink, M.J.: The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. *Thermochim. Acta* **404**(1–2), 163–176 (2003)

12. Yang, Z., et al.: Combustion behaviours of tobacco stem in a thermogravimetric analyser and a pilot-scale fluidized bed reactor. *Bioresour. Technol.* **110**, 595–602 (2012)
13. Mishra, R.K., Mohanty, K.: Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis. *Bioresour. Technol.* **251**(October 2017), 63–74 (2018)
14. Damartzis, T., Vamvuka, D., Sfakiotakis, S., Zabaniotou, A.: Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA). *Bioresour. Technol.* **102**(10), 6230–6238 (2011)
15. Sattar, H., Muzaffar, I., Munir, S.: Thermal and kinetic study of rice husk, corn cobs, peanut crust and Khushab coal under inert (N₂) and oxidative (dry air) atmospheres. *Renew. Energy* **149**, 794–805 (2020)
16. Arranz, J.I., Miranda, M.T., Montero, I., Sepúlveda, F.J.: Thermal study and emission characteristics of rice husk using tg-ms. *Mater. (Basel)* **14**(20) (2021)



A Systematic review of the BIM Methodology Applied to the Management and Sustainability of Hospital Centers. The Digital BIM Twin in the Management and Sustainability of Hospital Buildings. Case Study: University Hospital of Jaén

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Abstract. Due to the high technification of the health sector, it is expected that the future of hospital centers goes through the development of the concept of smart hospitals, where efficiency, safety and patient well-being must be highlighted as priorities. For this, it is necessary to develop and implement new and cutting-edge technologies that offer alternatives and solutions that improve the management, planning, analysis, design, development and operation of hospital buildings to make them more sustainable. To all this, we must add the high energy consumption of these buildings, due to their great activity that they carry out continuously (24/7/365), which also represents a great challenge to be able to decarbonize these buildings and make them more sustainable.

On the other hand, BIM (Building Information Modeling) is a collaborative work methodology for the management of building projects through a digital model (digital twin), which allows these projects, throughout their life cycle, to be more efficient and sustainable. Having the digital twin of the hospital building offers many possibilities for improvement in management and help to make decisions, such as: distribution and classification of spaces, organization of workstations, and services, preventive maintenance, integration with control systems, asset data, energy management, indoor air quality, safety, etc.

In this work, the experience of implementing the BIM work environment for the management and sustainability of an existing Hospital of more than 50 years old, such as the University Hospital of Jaén (HUJ), is shown.

Keywords: Hospital · hospital buildings · Health centers · BIM (building information modeling) · Smart buildings · Active management · Operation and maintenance · Energy efficiency · Sustainability · Decarbonization

1 Introduction

1.1 BIM (Building Information Modeling)

If we look around, technology is taking over our lives and the world. This technology needs information for the operation of management systems and models. This information is generated more quickly and in greater quantity.

Due to the high technification of the health sector, it can be expected that the future of hospital centers will go through the development of the concept of smart hospitals [1], where efficiency, safety and patient well-being must be highlighted as priorities. For this, it is necessary to develop and implement new and cutting-edge technologies that offer alternatives and solutions that improve the management, planning, analysis, design, development and operation of hospital buildings to make them more sustainable [2]. To all this, we must add the high energy consumption of these buildings, due to their great activity that they carry out continuously (24/7/365), which also represents a great challenge to be able to decarbonize these buildings and make them more sustainable [3].

On the other hand, BIM (Building Information Modeling) is a collaborative work methodology for the management of building projects through a digital model (digital twin), which allows these projects, throughout their life cycle, to be more efficient and sustainable [4, 5].

Then BIM is a methodology that allows you to manage the asset throughout its life cycle. Having the digital twin of the hospital building offers many possibilities for improvement in management and help to make decisions, such as: distribution and classification of spaces, organization of workstations, and services, preventive maintenance, integration with control systems, asset data, energy management, indoor air quality, safety, etc. This digital model of information allows **to simulate the real behavior of the building helping in the decision making of design and operation of the building**, not only for new buildings that must be, according to current legislation, buildings of almost zero energy consumption, but also for the rehabilitation of existing buildings.

1.2 BIM Dimensions

Within the BIM methodology, according to the uses for which it is intended, the following classification has been established [6] (Fig. 1):

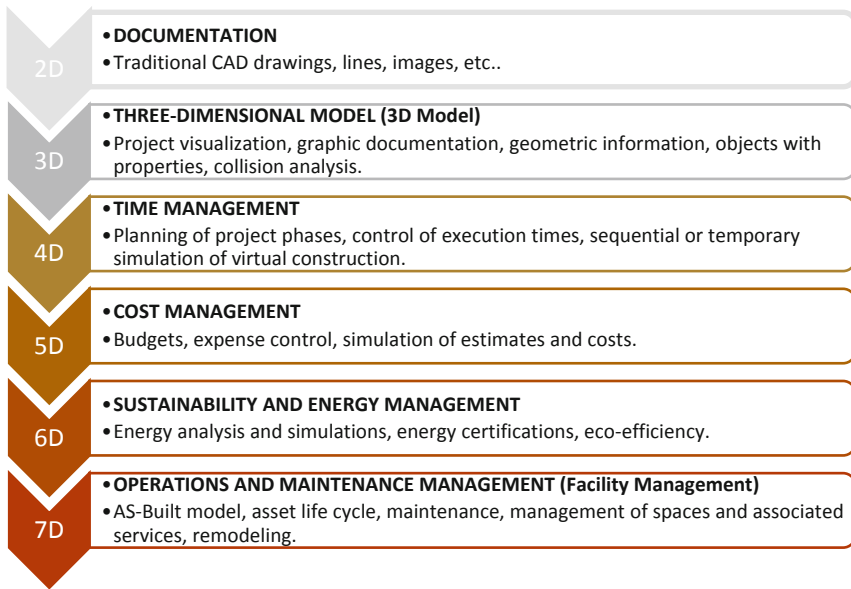


Fig. 1. BIM dimensions.

Currently we talk about the 8D dimension, Safety and health, as the analysis of risks in 3 dimensions.

1.3 Digital BIM Twin

This BIM methodology, in the operation phase (7D), adds value to all the Care Services provided by the Health Centers, allowing the support activities, organize and properly structure a large amount of data, through a single source of information that is the DIGITAL TWIN.

The BIM6D model allows to compare the existing state with the future state in terms of energy and economic balance, which will serve to study all the improvements as a whole [2], so that it is possible to select the alternatives of greater energy efficiency, lower environmental impact and greater comfort for the users of the building, which in turn will result in an improvement of the energy certification of the building.

In short, the digital twin allows architects, engineers, maintenance and operation managers, construction companies and maintainers to work on the same model, with updated and coherent information in a bidirectional way in the exchange of information [7].

1.4 Change of Technology

BIM is a methodology that integrates people, procedures and technologies.

This requires a change from the traditional way of working (Fig. 2).

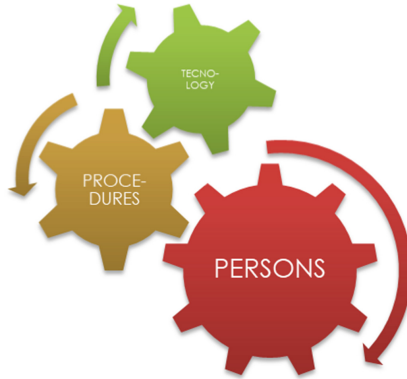


Fig. 2. BIM integrates people, procedures and technologies.

Adaptation to this new methodology requires: Un mental change in people; New processes: better document management, better communication (on-line, traceability) and technological adaptation; Training in new tools.

2 Object

In this work, the application of the BIM methodology to the Management (BIM7D) and Sustainability (BIM6D) of hospital buildings from the DIGITAL TWIN is studied.

Specifically, the building chosen is the Diagnostic and Treatment Center of the University Hospital of Jaén (Andalusian Health Service), which is 50 years old.

Through the DIGITAL TWIN of the building, it is intended to assess the use of the BIM model of the building for the Operation and Maintenance phase, energy management and its connection with the CMMS (Computerized Maintenance Management System).

3 Methodology

The BIM software used to obtain the architectural model has been REVIT (AUTODESK).

To do this, it was based on the plans of the building in “dxf” format, which served as a template for the construction of the geometry and BIM architecture of the Building through the REVIT program. Once the architectural model has been obtained, the distribution of areas and zonings is carried out according to the corporate CMMS, the materials of the thermal envelope of the building are configured, as well as the operational and occupational characteristics of all the spaces. Finally, the model is fed with available information from the different infrastructures and physical assets of the hospital, and the benefits of having a digital twin are studied and the possible connections with other modeling software, energy analysis, maintenance management, asset management, etc.

4 Case Study

The Diagnostic and Treatment Center of the University Hospital of Jaén, is a health center of the Andalusian Health Service, which belongs to the Ministry of Health of the Junta de Andalucía, located in Jaén. The construction of the building dates from 1972, as a specialized care center. The building, has as its main activity the attention of the external consultations of the Hospital and as a complementary activity in the building is community mental health and the archives in the basement of the building.

Description of the Building. The Diagnostic and Treatment Center of the University Hospital of Jaén (HUIJ), is located in a building of 1,000 m² of very elongated rectangular plant and has 6 floors built. The total constructed area is approximately 6,200 m². The 6 floors in which the building is divided are: Basement, Semi-basement, Low, and First to third. The building is made of reinforced concrete structure and the walls of the exterior envelope are exposed brick factory, have a half-foot chamber and a second plastered brick factory partition. The building's slabs are also made of reinforced concrete. The exterior carpentry is made of aluminum with 6 mm simple glass without breaking the thermal bridge. The interior distribution is made with plastered brick factory partitions. The main roof of the building is curved tile, gabled, not passable. The floors are terrazzo mainly. The coverings are ceramic in damp rooms, plastered and painted in the rest (Fig. 3).



Fig. 3. Overview of the Diagnostic and Treatment Center of the HUIJ.

Description of the Facilities of the Building. The production of cold for air conditioning is carried out by means of two chillers per direct expansion plant with ducts. Regarding the generation of heat, in order to supply hot water for air conditioning and domestic hot water, it is carried out by boilers fed with natural gas, which supply a series of water radiators located in all the perimeter areas of the building. The luminaires of the building are mostly fluorescent type, and do not have automatic control devices.

BIM Model of the Building. As mentioned above, in the first place, it was based on the plans of the building in “dxf” format, which served as a template for the construction of the geometry and BIM architecture of the Building through the REVIT program. Once the architectural model has been obtained, the materials of the thermal envelope

of the building, the operational and occupational characteristics of all the spaces are configured to obtain the energy model, also with the REVIT software. Figure 4 shows the BIM architectural model of the health center, which consists of 226 spaces, with 354 windows and 242 doors for example.

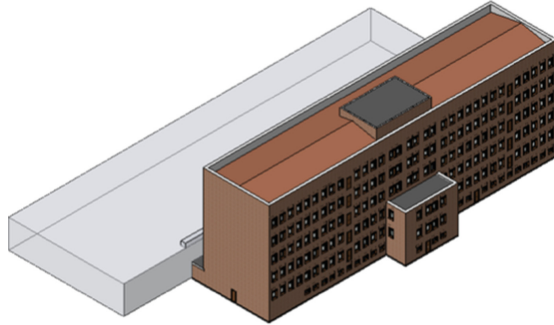


Fig. 4. Digital BIM twin of the building in REVIT.

It should be noted the difficulties to obtain the model as: Geometry (plans only of plant and not correctly updated); Thermal and energetic characteristics (mostly unknown, so they were estimated); Facilities. (modified and without properly updated documentation, most are hidden or difficult to access) (Fig. 5).

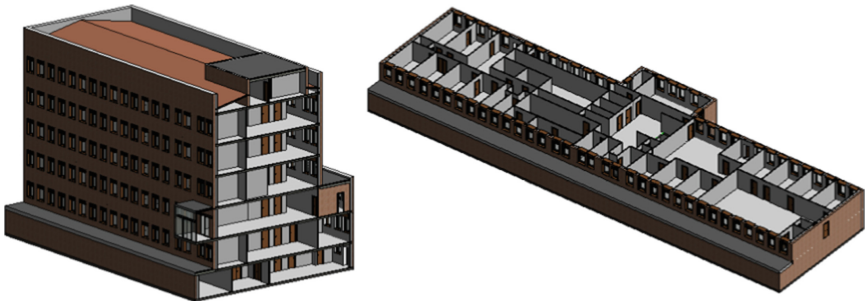


Fig. 5. Sections of the BIM model of the building in REVIT.

5 Results

Finally we obtain a digital twin of the hospital building as a single source of information for all the infrastructures of the hospital, as well as the energy simulation, which allows to improve the management throughout the life cycle of the building [8, 9], however, there are limitations and difficulties for the connection with other tools that allow the incorporation or extraction of information from the model (Fig. 6).

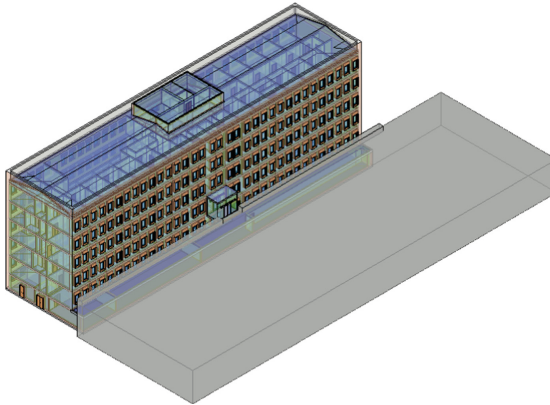


Fig. 6. BIM energy model of the building in REVIT.

5.1 Energy Simulation of the BIM Model with Revit Insight

The graph in Fig. 7, in the blue bar on the left, shows the energy consumption of the existing building modelled in BIM (259.11 kWh/m²/year). The following bars of the graph show the results of each of the improvements in the building, indicating in the blue bar the energy consumption of each new scenario resulting from applying the energy improvement, and in the orange bar is shown, the energy saved in relation to the initial situation of the existing building. Finally, the last bar on the right shows the combined result of all the proposed improvements, where a **total energy saving of 47% (120.94 kWh/m²/yr)** is achieved on the current situation of the Hospital. The improvements studied and indicated in the graph (from left to right) are: HVAC (high efficiency heat pumps); replacement of luminaires by LED technology; change of windows (double low emissive glass); installation of presence control systems and use of natural light to illuminate the building; improvement in installed electrical power by replacing more efficient

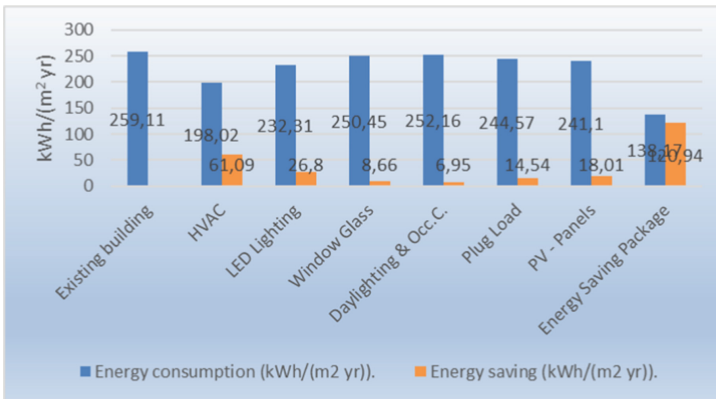


Fig. 7. Graph of the energy consumption and savings of the different scenarios of improvement of the energy efficiency analyzed for the building.

equipment (lifts, electro-medical equipment (RX), office equipment, etc.); installation of high-performance photovoltaic panels in 75% of the building's roof.

5.2 Contributions of the BIM Model Obtained

Structured and visual information by areas, classified by Management Units and Consumption Centers.

Physical activos located in areas and spaces, geolocated, with visual evidence.

Information of spaces: functional and occupational characteristics, zoning, typology, cleaning areas, thermal loads, ventilation needs, level of natural lighting, geometry and dimensions, characteristics walls, access restrictions, etc (Fig. 8 and 9).

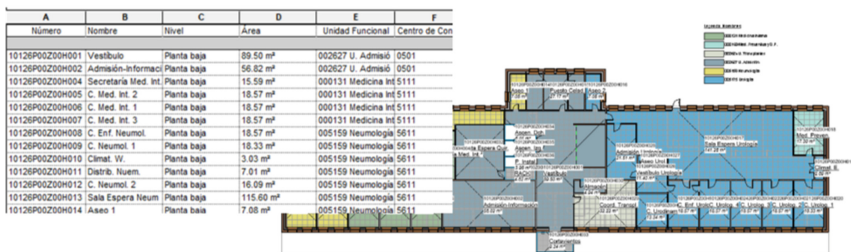


Fig. 8. Structured and visual information by areas, classified by Management Units and Consumption Centers.

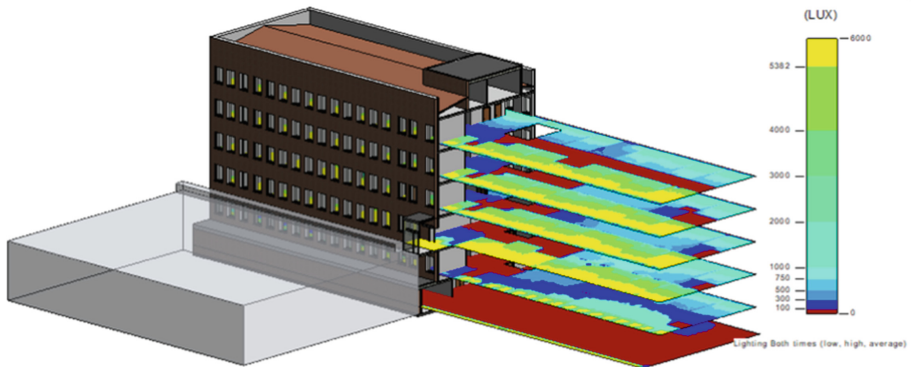


Fig. 9. Level of natural lighting per space.

Plans and updated graphic documentation to extract directly from the model: designation of spaces, CMMS locations, DIRAYA (electronic clinical history of the Andalusian health service) locations, classification of spaces, signage, key numbering, legionella locations, critical areas, fire sectors and evacuation plans, network points, wifi, telephony, cleaning areas, etc.

The model exportable to the “ifc” standard ready to be exploited with other tools.

In case of reforms, updated data of the model (geometry, assets, locations...) ready for incorporation into the different corporate tools (Fig. 10 and 11).

A	B	C	D	E	F	G	H	I
Número	Nombre	Nivel	Volumen	Ocupable	Tipo de acondicion	Carga de cale	Carga de refri	Sumatorio de
10126P00Z00H001	Vestibulo	Planta baja	231.13 m³	✓	Calentado y enfria	118 W	2371 W	180.1 L/s
10126P00Z00H002	Admisión-informa	Planta baja	178.98 m³	✓	Calentado y enfria	3049 W	9483 W	712.1 L/s
10126P00Z00H005	C. Med. Int. 2	Planta baja	58.48 m³	✓	Calentado y enfria	991 W	3146 W	235.7 L/s
10126P00Z00H006	C. Med. Int. 1	Planta baja	58.48 m³	✓	Calentado y enfria	991 W	3146 W	235.7 L/s
10126P00Z00H007	C. Med. Int. 3	Planta baja	58.48 m³	✓	Calentado y enfria	991 W	3146 W	235.7 L/s
10126P00Z00H008	C. Enf. Neuromol.	Planta baja	58.48 m³	✓	Calentado y enfria	1001 W	3147 W	236.0 L/s
10126P00Z00H009	C. Neuromol. 1	Planta baja	57.73 m³	✓	Calentado y enfria	1532 W	3213 W	245.7 L/s
10126P00Z00H010	Climat. W.	Planta baja	9.56 m³	✗	Sin acondicionar	No calculado	No calculado	No calculado
10126P00Z00H012	C. Neuromol. 2	Planta baja	50.69 m³	✓	Calentado y enfria	1479 W	1871 W	93.2 L/s
10126P00Z00H013	C. Sala Espera Neu	Planta baja	364.14 m³	✓	Calentado y enfria	5904 W	9774 W	535.0 L/s
10126P00Z00H014	Aseo 1	Planta baja	21.35 m³	✓	Ventado	907 W	1590 W	78.2 L/s
10126P00Z00H015	Puesto Celad.	Planta baja	81.94 m³	✓	Calentado y enfria	1943 W	3108 W	154.9 L/s
10126P00Z00H016	Aseo 2	Planta baja	21.35 m³	✓	Ventado	907 W	1565 W	62.5 L/s
10126P00Z00H017	Sala Espera Urolog	Planta baja	444.97 m³	✓	Calentado y enfria	5791 W	10388 W	596.6 L/s
10126P00Z00H018	Med. Preven.	Planta baja	54.48 m³	✓	Calentado y enfria	1568 W	1920 W	105.7 L/s
10126P00Z00H019	Climat. E.	Planta baja	8.47 m³	✗	Sin acondicionar	No calculado	No calculado	No calculado
10126P00Z00H020	C. Urolog. 1	Planta baja	57.73 m³	✓	Calentado y enfria	1529 W	3308 W	253.3 L/s
10126P00Z00H021	C. Urolog. 2	Planta baja	58.48 m³	✓	Calentado y enfria	991 W	3146 W	235.7 L/s
10126P00Z00H022	C. Urolog. 3	Planta baja	58.48 m³	✓	Calentado y enfria	991 W	3146 W	235.7 L/s

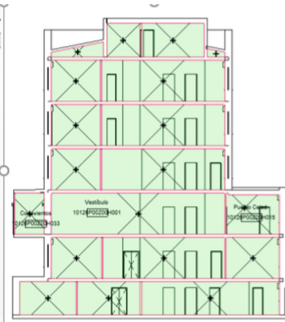
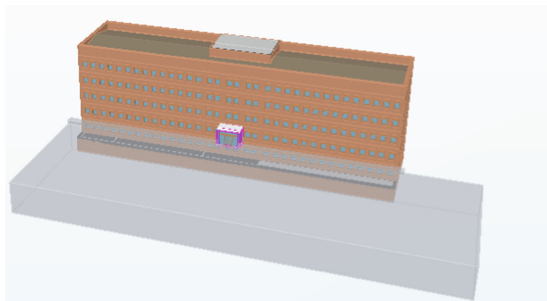


Fig. 10. Dimensions and volume of spaces with their functional and occupational characteristics, thermal loads, ventilation needs, etc.



```

Pset_SpaceCommon
Referencia: Cortavientos 10126P00Z00H033
Tabla de planificación de espacios
Ocupable: True
Aire exterior por área: 0
Reflectancia de muro: 0.5
Renovaciones de aire por hora: 2
Carga de climatización de diseño por área 0
Número: 10126P00Z00H033
Nombre: Cortavientos
Nivel: Planta baja
Volumen: 29.1 m3
Carga de calefacción calculada: 92381.6765024584
Carga de refrigeración calculada: 113630.753731217
    
```

Fig. 11. View in Tekla BIMsight of the BIM Digital Twin exported to the “ifc” standard with detail of space information.

6 Conclusions

With the results obtained in this work, it can be observed, how the digital twin offers a holistic and usable view of the information of hospital infrastructures, which imply benefits in general management and sustainability, since it offers the advantage of having centralized information, which allows saving time and optimizing resources, avoiding the accomplishment of repetitive tasks as happens when there are fragmented information sources. Obtaining the BIM digital twin of an existing building requires an economic effort that can be valued, but the cost of not having a BIM model is not valuable due to the GAP of productivity, and loss of information, which must be recovered repeatedly by different services, even more so taking into account that the exploitation and operation of a building represent, on average, between 75% and 80% of the total life cycle cost of a building.

The energy analysis of the BIM model of the building, allows to identify the most outstanding measures from the point of view of energy saving, as well as to discard other a priori interesting measures, which translates into a tool to help in decision making, and very to take into account when rehabilitating and modernizing a building, in addition to enabling quantifiable valuation criteria in administrative contracting, for the award of projects (new buildings and rehabilitation).


The digital twin BIM, through structured data associated with it, allows to add value to the set of Healthcare Services, by sharing updated information centrally, compared to the current work scenario where information is fragmented by different services. The digital BIM twin, a methodology that is here to stay, and transform the management of hospital buildings, although it requires a change of mentality that is never an easy task, much less when it is linked to a conceptual change.

References

1. Lin, C.-L., Chen, J.K.C., Ho, H.-H.: BIM for smart hospital management during COVID-19 using MCDM. *Sustainability* **13**, 6181 (2021). <https://doi.org/10.3390/su13116181>
2. Montiel-Santiago, F.J., Hermoso-Orzáez, M.J., Terrados-Cepeda, J.: Sustainability and energy efficiency: BIM 6D. Study of the BIM methodology applied to hospital buildings. value of interior lighting and daylight in energy simulation. *Sustainability* **12**(14), 5731 (2020). <https://doi.org/10.3390/su12145731>
3. Montiel-Santiago, F.J., Hermoso-Orzáez, M.J., Terrados-Cepeda, J., Paulo, B.: Analysis and energy certification of an Andalusian public health center. Comparative between the general option and simplified procedures. *Proceedings* **38**, 3 (2019) <https://doi.org/10.3390/proceedings2019038003>
4. Ferdosi, H., Abbasianjahromi, H., Banihashemi, S., Ravanshadnia, M.: BIM applications in sustainable construction: scientometric and state-of-the-art review. *Int. J. Constr. Manage.* (2022). <https://doi.org/10.1080/15623599.2022.2029679>
5. Vilutienė, T., Džiugaitė-Tumėnienė, R., Kalibatienė, D., Kalibatas, D.: How BIM contributes to a building's energy efficiency throughout its whole life cycle: systematic mapping. *Energies* **14**, 6680 (2021). <https://doi.org/10.3390/en1420668>
6. Piaseckienė, G.: Dimensions of BIM in literature: review and analysis. *Mokslas – Lietuvos Ateitis. Science – Future of Lithuania* **14** (2022). <https://doi.org/10.3846/mla.2022.16071>
7. Baarimah, A.O., Alaloul, W.S., Liew, M.S., Al-Aidrous, A.-H.M.H., Alawag, A.M., Musarat, M.A.: Integration of building information modeling (BIM) and value engineering in construction projects: a bibliometric analysis. In: 2021 Third International Sustainability and Resilience Conference: Climate Change, pp. 362–367 (2021) <https://doi.org/10.1109/IEEECONF53624.2021.9668045>
8. Wong, J.K.W., Zhou, J.: Enhancing environmental sustainability over building life cycles through green BIM: a review. *Autom. Constr.* **57**, 156–165 (2015). <https://doi.org/10.1016/j.autcon.2015.06.003>
9. Motalebi, M., Rashidi, A., Nasiri, M.M.: Optimization and BIM-based lifecycle assessment integration for energy efficiency retrofit of buildings. *J. Build. Eng.* **49**, 104022 (2022) <https://doi.org/10.1016/j.job.2022.104022>



Feasibility Study of the PET Fines Incorporation into Recycling Processes

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Abstract. Circular economy principles focus on the need to preserve natural resources and foster the use of environmentally sustainable practices. Concerning the use of plastics in a circular economy, increasingly demanding solutions have to be developed towards the zero-waste goal sought after by researchers and society alike. Particular attention has been put into the recycling of PET, mainly due to its wide spectrum of use and, consequently, to large volumes of related waste. The PET mechanical recycling process requires these waste materials to be shredded into PET flakes. Following such a procedure, these flakes are pelletized to be used again as feedstock. Considering the main stages of the mechanical recycling processes, which include plastic screening, shredding and washing, significant amounts of end waste materials are generated. This end-waste integrates small scale particles that are designated by plastic fines. Concerning the PET recycling process, the PET fines resulting from its mechanical recycling are not currently valued due to several technical issues, such as their high contamination level and the complexity of sorting them from other small-size particles. Current research focuses on the feasibility of incorporating these PET fines into the film/injection extruders, avoiding this way the need for an intermediate pelletization stage. To allow for such direct incorporation of PET fines into recycling processes, different decontamination and sorting solutions were implemented and tested. The current study is based on analyzing the mechanical properties of PET fines, using laboratory tests such as FTIR, DSC, MFI, moisture content, tensile tests and bending tests. Preliminary results allow foreseeing the successful direct incorporation of PET fines into PET recycling.

Keywords: Plastic · Recycling · Circular economy · PET fines

1 Introduction

Since the 1970s, when the concept of sustainable development was first introduced by United Nations Conference on the Human Environment [1], there has been a significant effort to find alternatives to existing products and processes to promote not only sustainability but also the circular economy, as both of these notions are key to foster sustainable development in our current and future society.

Among the various alternatives to the linear economy principles of take-make-dispose, the circular economy concepts of recycling and reuse are by far more sustainable. Thus, the ability to use waste materials to be transformed into new raw materials for the process brings positive impacts to all three main perspectives of sustainability, namely the economic, social, and environmental dimensions [2].

Particularly, when trying to apply the concepts of sustainability and circular economy to the plastics sector different challenges arise. Nonetheless, such efforts are critical since the plastics industry is one of the fastest-growing in recent years, with all the benefits and drawbacks of conventional and advanced manufacturing processes [3]. Again, one of the most promising solutions to be adopted to promote the sustainability of plastics is recycling [4].

When looking at the plastics industry, it's unavoidable to look for improvements in processes and alternatives that use fewer resources and/or allow these resources to be reintegrated into the production chain due to the production circumstances, which include the use of petroleum shunt raw material and its scarcity.

Even in the recycling chain, there is waste produced and some sub-materials that are not used during the process, thus generating by-products that don't get valued or reused. PET fines, which are the consequence of the breakage and washing of PET during its recycling process, are among those whose economic and energetic potential has not been considered in current value chains and that also can have harmful impacts on the environment [5]. The amount of PET fines generated from the mechanical recycling of PET bottles can reach 2 to 5% and from the mechanical recycling of PET trays can reach up to 20 to 30%. Because of their small size, these microplastic fines are not currently recycled with PET flakes, which result from the recycling of PET bottles.

As a result of the challenge of finding alternatives that allow integrating the highest amount of waste to be reused in the material recycling of PET while also optimizing the recycling process to minimize unwanted by-products, the current research focuses on characterizing the PET fines to study their properties and to discuss the feasibility of reintroducing this waste material into the production cycle.

2 PET Fines from Plastics Recycling

Plastics have become increasingly valuable since their discovery, serving as a cost-effective solution in a variety of industries, including construction, automotive, electrical and electronics, agricultural, domestic use, and packaging, among many others. So much so that, despite the 2020 crisis, Europe's plastics manufacturing dropped by barely 5%. And, while this figure appears significant, given that 58 million tons of plastics were manufactured in 2019 and 55 million tons in 2020, these figures can still be regarded

as very high. It's also worth noting that these figures just pertain to Europe; they don't necessarily imply that the scale has shrunk globally, given China's increase from 31% to 32% of global plastic manufacturing, as well as North America [6].

However, due to its future productivity shortfall, as well as the harm caused by high persistence under abrasive conditions, which transforms plastic into microplastics (plastic pieces smaller than 5 mm), it was decided that the Member States of the European Union (EU) should reduce disposable plastic consumption [7] and improve plastic waste management [8, 9].

According to Plastics Europe [10], to promote better waste management, more than 29 million tons of post-consumer plastic waste was collected in the EU27+3 in 2020. Nevertheless, only a third were delivered to recycling facilities within and outside the EU27+3, about 23% were sent to landfills and more than 40% were sent to energy recovery operations.

Given that the packaging industry produces around 40% of the total plastic waste, additional attention must be paid to encouraging recycling in this sector [10].

However, there are still many difficulties to be overcome in the recycling process. One of them would be, according to Elamri *et al.* [11], the fact that the post-consumer PET suffers during the recycling process: thermal exposure and shear degradation with the simultaneous presence of retained moisture and physical contaminants which lead to a significant average macromolecular weight loss during reprocessing at high temperatures, resulting in reduced mechanical properties. Besides, the intensive cleaning and drying of PET flakes before extrusion, the sorting of impurities and the use of chain extenders or modifiers are options to improve those properties.

Another relevant point is that PET fines are generated during the recycling operations, which are smaller fractions than flakes and are a by-product resulting from the shredding of the materials. Therefore, it can be inferred that there will be even greater structural and mechanical differences between PET fines and PET flakes. It has also to be noticed that PET fines cannot be included in the recycling process, as they melt before the larger dimension flakes, making material flow difficultly when producing pellets of rPET [12]. In other words, as these differences become greater and more evident, it requires increased effort on the search for solutions that make it possible to incorporate PET fines into recycling processes.

In a nutshell, it is key to look for ways to reuse this type of by-product materials from the PET recycling process to limit the amount of non-recycled PET and therefore contribute to the circular economy principles.

3 Experimental

3.1 Material

In this study, the sample of PET fines was collected after washing, in the drying process, resulting from several stages of the mechanical recycling of PET post-consumer waste. The mechanical recycling system is composed of NIR and manual sorting, shredding, washing and drying. These samples are known to contain contaminants such as different types of polymers, metals, and small pieces of wood. The maximum dimension of the PET fines is 4 mm.

It was important to conduct multiple tests to characterize the samples to gain a better understanding of their composition and, as a result, find acceptable methods to promote recycling. Initially, contaminants in the samples were examined. A sample of roughly 10 g of material was separated, measured on a precision balance from Precisa, model 262SMA-FR, and evaluated by manually removing metals, wood, colored and yellowish components, using tweezers, to get a sample just with white and blue PET material.

3.2 Density

Several tests were carried out to determine the density using the pycnometer method. The solvent was water at 23 °C with a density of 0.99751 g/cm³. The mass of sample and water in the pycnometer of solids were measured on a precision balance from Precisa, model 262SMA-FR and the density was calculated by Eq. (1).

$$\text{Density} = \frac{m_{pic+sam} - m_{pic}}{\frac{m_{pic+w} - m_{pic}}{d_w} - \frac{m_{pic+sam+w} - m_{pic+sam}}{d_w}} \quad (1)$$

where m_{pic} is the mass of dried pycnometer of solids, $m_{pic+sam+w}$ is the mass of pycnometer with sample and water, $m_{pic+sam}$ is the mass of pycnometer with sample, m_{pic+w} is the mass of pycnometer full of water and d_w is the density of water at 23 °C.

3.3 Moisture Content

The subsequent set of tests followed the procedures outlined in ISO 15013:2007 [13] to determine the moisture content in the samples. The method is based on the gravimetric method by the measurement of the variation of mass between the mass of the sample as received and the mass of the sample after drying at 105 °C for 24 h. The mass was measured at ambient temperature with a precision balance from Precisa, model 262SMA-FR.

3.4 Melt Flow Index

The Melt Flow Index (MFI) was carried out at 265 °C, using ATS Faar equipment, according to the procedure prescribed in ISO 1133-1:2011 [14] with the 2.16 kg of weight to force the sample to flow through the flow chamber. To adapt the standard to the given experimental flow, the method was modified for 10 g of sample to be inserted into the equipment and a cutting time of 25 s.

3.5 DSC Analysis

The equipment DSC131 from Setaram Instrumentation was used to perform the Differential Scanning Calorimeter (DSC) analysis, test for determining thermal characteristics, glass transition temperature, T_g , crystallization temperature, T_c , melting temperature, T_m , and crystallinity, X_c %. The results were obtained after the second scan with a temperature range from 30 °C to 300 °C, without purge gas, with a scanning speed of 10 °C/min and sample weight ranging between 30 mg and 35 mg. The crystallinity was calculated based on the heat of fusion of 100% crystalline PET of 120 J/g.

3.6 FTIR

The presence of additives and contaminants, including polymers and monomers, was analyzed using the FTIR technique (Fourier-transform infrared spectroscopy). This technique allows identifying the composition of a material with high levels of precision. The FTIR spectrometer used was the Spectrum Two from PerkinElmer and the resulting spectrum was studied using the software Spectrum IR, in a multisearch analysis.

3.7 Bending and Tensile Tests

Bending and tension tests were also undertaken to characterize the mechanical properties of the samples, which were preceded by a step of specimen preparation in which 3.30 kg of dried PET fines were injected at two different pressures, 60 bar and 80 bar, at a temperature of 140 °C. The mold used to inject is in accordance with standards for 3-point bending and tensile tests, the ASTM D638 standard [15]. The 3-point bending tests were carried out using a Zwick/Roell Z100 universal test machine in accordance with the ISO 178:2003 standard [16], with a test speed of 5 mm/min, a load cell of 100 kN, and a distance between supports of 68 mm.

4 Results Discussion

According to the procedures presented in the previous section a set of tests was carried out to characterize contaminants in the samples, densities, moisture content, melt flow index, DSC, FTIR and tensile and bending tests.

Table 1 presents the analysis of visible contaminants on the samples, which were sorted by the manual removal method.

Table 1. Analysis of visible contaminants on the samples.

Test	Material	Mass (g)	Relative weight (%)
1	Metals and Wood	0.047	0.5%
	Miscellaneous materials	0.278	2.7%
	Blue and White	9.708	95.4%
	Yellowish	0.162	1.8%
2	Metals and Wood	0.242	2.1%
	Miscellaneous materials	0.271	2.9%
	Blue and White	9.420	93.5%
	Yellowish	0.140	1.5%

As a result of the foregoing analysis, it was possible to observe that most of the samples were composed of white and blue plastic. Nevertheless, a significant percentage of metal contaminants and pieces of wood were identified as specimen contaminants in various amounts. Other contaminants identified in the analyzed specimens relate to different percentages of various polymers that may be recognized and distinguished by their colors, as well as yellowish materials that indicate the presence of polyolefins.

Table 2 presents the density and moisture content of PET fines, measured in triplicate, according to the methods described in Sects. 3.2 and 3.3.

Table 2. Density and moisture content of PET fines.

Test	Density (g/cm ³)	Moisture content (%)
1	1.062	0.65
2	1.295	0.62
3	1.277	0.65

It can be observed from the results presented in Table 2 that the density of the samples is consistent, but they differ from the density values for virgin PET, which has values between 1.29–1.43 g/cm³ [17]. This can be explained by the presence of polymers like polystyrene and polyolefins and/or additives that can decrease the density of the sample.

It can be observed from Table 2 that the two tests had approximately the same moisture content. However, given the variability of the sample, a margin of 5% error level can be considered acceptable.

Table 3 presents MFI results, which were conducted using the procedure prescribed in ISO 1133-1:2011 and it was carried out at 265 °C, as described in Sect. 3.4.

Table 3. MFI results of PET fines.

Test	MFI (g/10 min)
1	355.72
2	191.02
3	67.250
4	50.866
5	82.094
6	88.238

The MFI results allowed identifying that the material under research had particles beyond the visible spectrum, given that the findings differed significantly from what had been expected based on the literature [18], which indicates that ground bottles have a Melt Flow Index of 15.98 g/10 min.

It should be noted that tests 1 and 2 of Table 3 were conducted without any contaminant removal treatment, with results that were about 12 to 22 times higher than expected. This may be due to the presence of metals and wood particles, which could disrupt the flow of the material due to the obstruction of the nozzle at the end of the flow chamber of the MFI equipment. Metal and wood contaminants were removed from Tests 3 and 4 as the initial step and the results were 3 to 4 times higher than expected. In tests 5 and 6, all visible contaminants were removed and the sample was the same as the one used for the contamination analysis where the fraction of white and blue plastics was used. The results of tests 5 and 6 are more consistent but still around 5 times higher than expected. Nevertheless, there should still be a significant presence of impurities, additives, or multilayer material, which would explain the wide range of readings. In addition, the irregular shape of the input material with lower dimensions in comparison to those of the pellets, that are usually used to measure MFI, may affect the final output.

Table 4 presents DSC results for 3 tests, in which T_g refers to the glass transition temperature, T_c refers to crystallization temperature, T_m refers to melting temperature and X_c % the crystallinity of PET fines.

Table 4. DSC results of PET fines.

Test	T _g (°C)	T _c (°C)	T _m (°C)	X _c %
1	97.97	161.76	267.10	12
2	102.62	156.92	269.60	5.1
3	99.52	157.25	265.71	10

The reported results in the literature [19] refer that the virgin PET has a glass transition temperature of 72.8 °C, a crystallization temperature of 135.7 °C and a melting temperature of 251.9 °C. However, the tests have divergences from the reported values, according to the DSC test analysis. It is possible to infer from the readings obtained in Test 2 as being the result of a non-fused particle, *i.e.*, a plastic substance that could not reach the melting point at 300 °C. On what concerns Test 3, since there are more colored materials, *i.e.*, materials that are not PET, thus having different values than expected.

Figure 1 shows the graph of heat flow versus temperature resulting from the DSC analysis of the PET fines.

In accordance with the presented in Fig. 1, the values were consonant with each other, however, it can be observed that there are differences in the graph which, as mentioned above, can be explained by the presence of other materials besides PET.

According to the FTIR analysis, most of the samples contain more than one layer of polymer and/or present additives or contaminants (80% of the samples), as well as materials that do not contain PET at all (16%) and only 4% of the samples analyzed were made entirely of PET, as shown in the chart of Fig. 2.

The FTIR tests also showed that Vinyl Acetate, Adhesive of Vinyl Chloride, Poly(trimethylene terephthalate (PTT), Poly(Phenylene Disulfide) and Quaternized Polyimidazoline are some of the components found in the analysis, here referred to as PET +, in reference to the presence of additives.

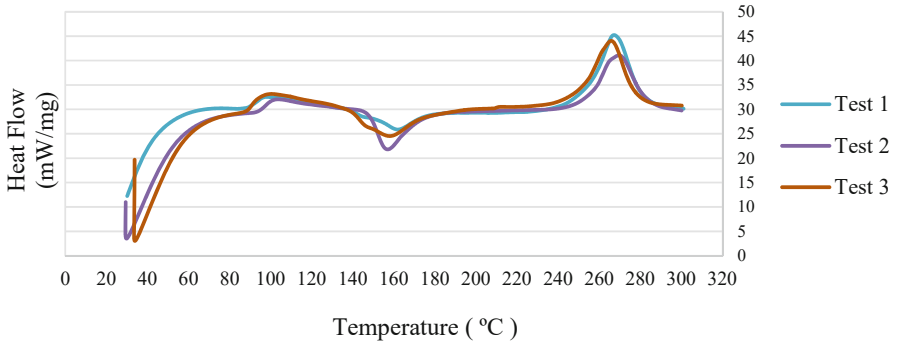


Fig. 1. DSC analysis of the PET fines.

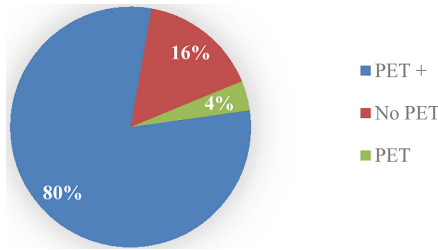


Fig. 2. Percentage of PET, PET samples with multilayers and/or contaminants and additives and non-PET materials.

On what concerns the mechanical characterization of the sample materials, 3-point bending tests were performed with the specimens injected at 60 and 80 bar and the results are presented comparatively in Fig. 3.

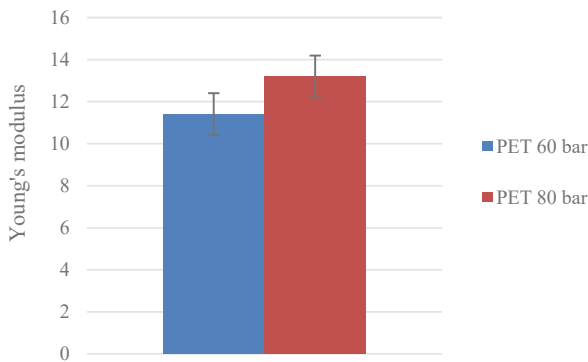


Fig. 3. Comparative graph of bending tests with specimens injected at 60 bar and 80 bar.

In Fig. 3 it can be seen that Young's Modulus has similar values for injection at 60 bar and 80 bar, indicating that there are no significant differences regarding the

injection pressure used. On what refers to the virgin material, the values found are above expectations, considering that, according to the literature, the values should oscillate between 2.76 and 4.14 Gpa [20].

Figure 4 shows the stress and strain curves until the limit of the fracture of samples of PET fines injected at 60 bar and Fig. 5 shows the stress and strain curves until the limit of the fracture of samples of PET fines injected at 80 bar.

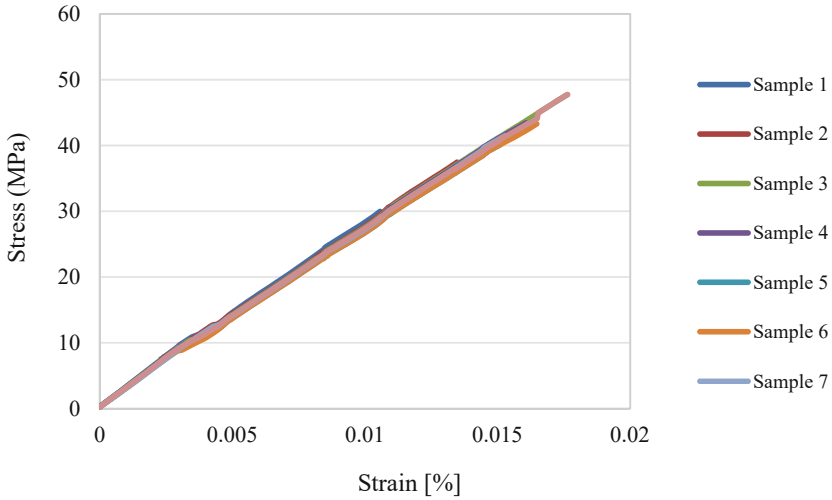


Fig. 4. Stress-strain curve of PET fines injected at 60 bar.

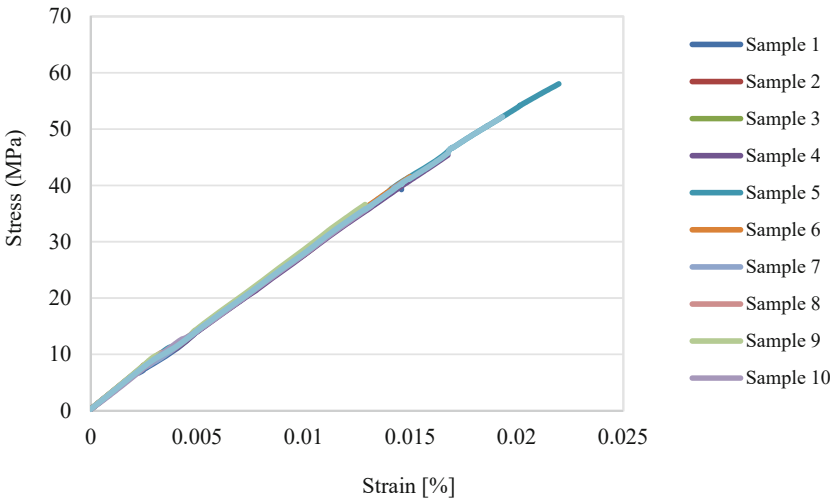


Fig. 5. Stress-strain curve of PET fines injected at 80 bar.

The specimen has a very low deformation with no significant differences regarding injection pressure.

The values found for both the 60 bar and the 80 bar samples are quite different from the values reported in the literature [18] for virgin PET, given that they support a maximum strain between 50 and 60 MPa, with a strain of more than 30%. It is also worth noting that the curves don't match those predicted from a PET-only material, and the material doesn't yield, making it impossible to determine its yield strength. This indicates the sample's brittleness by the fact that it breaks before yielding.

5 Summary and Discussion

The tests conducted with the PET fines collected after washing and drying PET residues resulting from several stages of the industrial recycling of PET post-consumer waste allowed finding that despite the number of visible contaminants found being relatively small (5%–7.5%), the presence of additives found from FTIR in the fraction of PET and other polymers that resemble PET is significant and may be the explanation for a large part of the differences in values found, as density, which has lower values because the polymers present have lower densities than PET, such as polystyrene and polyolefins.

The MFI values were substantially higher than expected according to the literature [18], in which the values should be close to 30 g/10 min. However, this result can be explained both by the material not being entirely composed of PET and by its smaller dimension than the standards, which facilitates its fusion.

On what concerns the DSC tests, the results showed to be higher than expected according to the literature [19], but the generated curves are similar to the pattern found in virgin PET. The crystallinity is significant, and it can contribute to increasing the stiffness found in the bending and tensile tests. The specimens for the bending and tensile tests were not subjected to DSC analysis but were injected into the mold at ambient temperature. In order to decrease the stiffness and avoid the crystallinity, the mold could be refrigerated to about 8 °C. On the other hand, refrigeration would increase the need for energy in the production of the specimen.

Finally, on what refers to the mechanical properties, the bending and tensile tests showed no significant differences regarding the injection pressure of the molds, but as there are large differences when comparing the results expected for virgin PET, being much more rigid, residual deformation and do not show yield.

6 Conclusion

One of the methods to increase the material's circularity is by improving its recyclability, thus extending its life. Nonetheless, the mechanical recycling of plastics must be improved to avoid significant amounts of rejected material. In the PET recycling process, after automatic and manual sorting, washing and drying, the sieving gets about 2 to 5% of PET fines, which are particles smaller than 4 mm. These PET fines are contaminated with metal, wood, sand, additives, organic contaminants, and other polymers in addition to PET.

In this study, several characteristics of the PET fines were assessed using different methods, such as FTIR, DSC, MFI, moisture content, tensile tests and bending tests.

The contaminants (metal, wood, yellowish and miscellaneous materials) were evaluated and although they are about 5%, they strongly affect the mechanical and thermal characteristics. Besides the contaminants, polymeric multilayers on the PET fines were detected by FTIR. This allows assuming that they can contribute to the deviation of the mechanical and thermal characteristics of PET fines when compared to virgin PET.

Given that the material analyzed is obtained from post-consumer packaging bottles, which still have labels attached to them, it's also possible to infer that the contaminants found in the samples are from such labels, which may not have been removed completely. Therefore, considering these results it is not possible to directly insert PET fines into recycling processes, given the significant differences in physical and mechanical properties when compared to virgin PET. Based on these results, the increase of the intrinsic viscosity may not be enough to successfully recover the PET fines properties.

It is recommended that to provide improvements to the material properties, the PET fines are subjected to a separation process to remove metal, wood and miscellaneous material, in order to obtain samples with a high degree of PET and multilayer material.

More research is needed to develop efficient methods to separate contaminants that, as known, are below 4 mm and magnetic, NIR sorters and others have limitations. Another recommendation would be the assessment of an additional step of mechanical drying before shredding to minimize fines production, although further research is required to quantify this aspect.

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References

1. United Nations Organization: Stockholm 1972 - Declaration of the United Nations Conference on the Human Environment (1972). www.unep.org. Accessed 11 Apr 2022
2. Shamsuyeva, M., Endres, H.J.: Plastics in the context of the circular economy and sustainable plastics recycling: comprehensive review on research development, standardization and market. *Compos. Part C: Open Access* **6**, 100168 (2021)
3. Baldassarre, B., Maury, T., Mathieux, F., Garbarino, E., Antonopoulos, I., Sala, S.: Drivers and barriers to the circular economy transition: the case of recycled plastics in the automotive sector in the European Union. *Procedia CIRP* **105**, 37–42 (2022)
4. Demets, R., van Kets, K., Huysveld, S., Dewulf, J., de Meester, S., Ragaert, K.: Addressing the complex challenge of understanding and quantifying substitutability for recycled plastics. *Resour. Conserv. Recycl.* **174**, 105826 (2021)
5. Kershaw, P., Rochman, C.: Sources, fate and effects of microplastics in the marine environment: part 2 of a global assessment. In: GESAMP (2016)
6. Galileu, R.: Revista Galileu (2021). <https://revistagalileu.globo.com/Um-So-Planeta/noticia/2021/06/producao-de-plastico-em-2020-diminuiu-pela-primeira-vez-desde-2008.html>. Accessed 11 Apr 2022
7. European Parliament: Directive (EU) 2019/904 of the European Parliament and the Council of 5 June 2019 on reducing the impact of certain plastic products on the environment (2019)
8. European Parliament: Directive 94/62/EC of 20 December 1994 on Packaging and Packaging Waste (1994)

9. European Commission: Waste Framework Directive (2018)
10. Plastics Europe: Plastics-the Facts 2021 An analysis of European plastics production, demand and waste data (2022). <https://plasticseurope.org/>
11. Elamri, A., Abid, K., Harzallah, O., Lallam, A.: Characterization of recycled/virgin PET polymers and their composites, **3**(4–1), 11–16 (2015)
12. Spinacé, M., De Paoli, M.: A Tecnologia da Reciclagem de Polímeros, *Química Nova* (2005)
13. International Organization for Standardization: ISO 15013:2007 - Plastics—Extruded sheets of polypropylene (PP)—Requirements and test methods (2007)
14. International Organization for Standardization: ISO 1133-1:2011 - Plastics—Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermo-plastics—Part 1: Standard method (2011)
15. A. S. F. T. A. Materials: ASTM D638 - Standard Test Method for Tensile Properties of Plastics (2014)
16. International Organization for Standardization: EN ISO 178:2003/A1:2005 - Plastics - Determination of flexural properties - Amendment 1: Precision statement (ISO 178:2001/A1:2004) (2004)
17. Freixa, F., Alves, J.L., Rangel, B.: Design de novos produtos com reciclagem de PET. In: 8º Congresso Luso-Moçambicano de Engenharia / V Congresso de Engenharia de Moçambique (2017)
18. Oliveira, E.J.G.: Estudo sobre a processabilidade de PET reciclado obtido pelo processo de reciclagem mecânica, Universidade do Minho (2016)
19. Santos, A.C., Silva, L.G.A.: Reciclagem do PET pós-consumo e estudo do efeito da radiação ionizante em suas propriedades. In: 18º CBECiMat - Congresso Brasileiro de Engenharia e Ciência dos Materiais, Porto de galinhas, Brasil (2008)
20. Sonelastic: Modulus of elasticity and Poisson's coefficient of polymeric materials, 22 April 2022. <https://www.sonelastic.com/en/fundamentals/tables-of-materials-properties/polymers.html>



Ink Removal on Plastic Films Printed by Flexography

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Abstract. Plastics are key engineering materials for our society and economy, mainly due to their multifunctionality and ease of processing. Nonetheless, their main drawback is related to the fact that when these cannot be reprocessed, they do generate waste, which leads to several environmental impacts. Therefore, considering plastics' circularity, minimizing their waste, and the resulting impacts, stresses the need for these to be recyclable. One of the main challenges that concern their recyclability is the deinking of plastic films when printed by flexography. The current technology uses non-bio-based surfactants and non-renewable surfactants, which are harmful to the environment. Therefore, the main objective of current research is to develop an environmentally sustainable process for ink removal on printed post-industrial flexible plastic films using bio-based surfactants. This process focuses on obtaining a deinked plastic that may be reprinted, avoiding this way for inappropriate disposal or reprocessing problems. The value increase of upcycling such post-industrial waste makes it possible to match the quality of the virgin plastic, which is key to carrying out an effective cost analysis of recycled plastic when compared to the new plastic films. Dedicated laboratory deinking procedures were undertaken with transparent polyethylene films printed by flexography with different conditions. Preliminary results show the dedicated experimental ink removal procedure using bio-based surfactants to be effective and environmentally sustainable.

Keywords: Plastic film recycling · Biobased surfactants · Deinking · Solvent-based ink · Cationic surfactant

1 Introduction

Plastic packaging accounts for approximately 40% of worldwide plastic use [1], with the corresponding waste posing a significant threat to nature and the environment, thus requiring the adoption of a greener, circular economy centered on waste avoidance and recycling [2]. As a result of such increased plastic usage, there is a corresponding exponential growth in plastic waste, which leads to greater demand for natural gas and oil as raw materials for plastic manufacturing [3]. Due to the general demand for raw materials, environmental concerns, and solid waste considerations, recycling plastic film from industrial and household waste streams is becoming ever more important [4].

Most of the plastics currently used are almost completely derived from petrochemicals produced from fossil oil and gas. Thus, to manufacture these plastics, significant amount of energy is required, which leads to a high consumption of corresponding volumes of fossil fuels [5]. To minimize the effect of raw material depletion the combined use of recycled and virgin plastics leads not only to minimize energy consumption and reduce environmental impacts, but also, in some cases, to improve their properties [6].

Plastic film waste has a variety of negative environmental consequences and is a high concern for the consumer goods industry, as large quantities of scrap plastic films are currently disposed of in landfills or incinerated [7]. Effective film deinking technology is a promising alternative to conventional recycling of plastic films as it allows for the reuse of scrap plastic films usually disposed of as industrial waste [8].

The deinking of plastic films produced by flexography is one of the most significant barriers to their recyclability as the current technology relies on non-biodegradable and non-renewable surfactants, which are harmful to the environment [9]. This severe constraint in the recyclability of plastic films requires urgent action to identify sustainable alternatives to the current deinking processes. Consequently, the primary goal of this research is to analyze and discuss the use of bio-based surfactants for ink removal on printed post-industrial flexible plastic films. In this research, the use of aqueous bio-based surfactant solutions for plastic film deinking was analyzed and discussed, since these surfactants are more environmentally friendly [10].

2 Deinking of Plastic Films

The conventional methods for deinking plastic films are mostly based on non-biodegradable and non-renewable surfactants, which require complex procedures that result in hazardous waste with negative impacts on the environment [4]. Most of the surfactants on the market are synthesized from petrochemical products [11]. However, the desire to reduce the use of products that are harmful to human health and the environment has led to the development of green surfactants, which are surfactants that are formulated with natural, biodegradable surfactant components of biological (plant or microbiological) origin or chemically synthesized from natural raw materials [12].

2.1 Bio-Based Surfactants

In the case of printed packaging, the presence of printing ink during mechanical recycling is a major issue that has a significant negative influence on the process. Given this,

research has often been conducted to develop more efficient ways to remove ink from plastics [8]. In this quest, it may be pointed out that aqueous surfactant solutions are considered suitable choices for such work because of their biodegradability, non-toxicity, and non-volatility [3].

The use of natural compounds instead of chemical surfactants has been explored due to their environmental sustainability and low toxicity, as well as a range of additional advantages [12]. These bio-based surfactants, also often referred to as green surfactants, are acknowledged to be the next generation of industrial surfactants, as they meet most of the requirements for low environmental impact solutions [13]. Bio-based surfactants are key in the current research effort towards greening industrial processes, as these compounds may be considered environmentally friendly due to their low (or absent) toxicity and high biodegradability [14].

The term bio-based surfactant refers to a surfactant produced by a chemical or enzymatic process that uses renewable substrates as raw materials [15]. According to ISO/DIS 21680, a bio-based surfactant is defined as a surfactant wholly or partly derived from biomass (based on biogenic carbon) [16]. Because bio-based surfactants frequently require extra features to increase their functional qualities, combining bio and petroleum-based feedstocks has been one approach for overcoming some of the green surfactants' functional constraints [15]. To support analyzing the bio-based surfactants' sustainability standards, the European Commission of Standardization in its EN 17035:2021 standard has defined categories for biosurfactants, including >95% totally bio-based, 50–94% majority bio-based, 5–49% minority bio-based, and 5% non-bio-based [17].

2.2 Ink Removal on Plastic Films Using Bio-Based Deinking Agents

When recovering rigid plastics or plastic films, deinking is a critical step toward valuing plastic waste in subsequent mechanical recycling stages. Considering that during their production operations, plastic film industries generate between 8% and 12% of printed scrap [8], it is key to develop and implement sustainable solutions to improve the circularity of such post-industrial waste.

On what refers to plastic films, such deinking even allows for recovering unwound film rolls to be reprinted and reused. To such an end, innovative solutions by Piolat [18] and Gamma Meccanica [19] allow foreseeing sustainability benefits by valuing post-industrial waste into new raw materials without the need for recycling, or to further value its recirculation. Nevertheless, such solutions still provide for revalued raw materials with low mechanical and optical properties [8].

Deinking, which involves the removal of various colors and layers of ink from the plastic film, might be considered a laundering process, as it requires the removal of ink from the surface, which is adhered to it by Van-der-Waals, electrical, and mechanical forces [4]. As above mentioned, most of the current deinking procedures for plastic films use non-biodegradable and non-renewable surfactants [4]. Nevertheless, increased research effort is being put towards the use of bio-based agents in the deinking of plastic films [4, 20, 21]. Furthermore, biosurfactants are more effective in reducing surface and interfacial tensions than synthetic counterparts, and they can withstand high temperatures as well as extreme pH and ionic strength [20].

To analyze and discuss the deinking efficiency on plastic films, different parameters and variables must be addressed. The performance of the deinking agent depends on many aspects like pH and temperature [3], type and concentration of the deinking agent [21], or time and mechanical action [4]. Therefore, to study the removal of ink from printed plastic films it is key to consider the impact and effects of such process variables.

3 Materials and Methods

3.1 Materials

For this study, samples of a colorless clear transparent polyethylene film, printed by flexography with different conditions were analyzed. The clear transparent LDPE film was printed for commercial purposes with a final layer of 50 μm thickness. The printed film prints are constituted by the intermediate combined intermediate layers presented in Table 1.

Table 1. Summary of the print layers of the current case study.

LDPE film print
White
Yellow
Magenta
Black
Green
Blue

To perform the deinking of plastic films, surfactants may be needed to reduce the surface or interfacial tension at the air/water, ink/water, and plastic/water interface, and this can increase the wettability of the solution and allow alkali to penetrate between the ink particle and the plastic film. The surfactant used in this case study was the BIO 691 from the Bioloop product family, manufactured by Lankem Ltd. (UK). It is bio-based and, therefore, is not harmful to the environment, according to the EC regulation no. 1272/2008. The surfactant was used as supplied and diluted on deionized water for the testing conditions at approximately pH 8.

3.2 Deinking Tests

To carry out the experimental deinking test procedures, a total of 16 subsamples were cut into approximately 1 by 5 cm long strips. These tests were performed to collect results for 4 factors: Surfactant concentration, bath temperature, bath time, and brushing.

Half of the plastic film strips were submitted to a set of experimental deinking test procedures at room temperature, whereas the remaining samples were tested at 40 °C.

With the use of a 1–5 mL M5000 adjustable volume manual pipette, tweezers, test tube, glass beakers, digital thermometer and a RCT Basic Safety Control magnetic agitation plate, the samples were submerged in each test tube of 30 ml for the 30 s and 1 min tests. The surfactant solutions of 5% and 2.5% were freshly prepared with distilled water for each sample, and the pH level of the aqueous surfactant solution was not adjusted. The samples were agitated using the magnetic stirrer.

After draining, the film strips were submitted to brushing, washed with water, and dried. The 16 plastic film strips were randomly collected to analyze the level of deinking. Each processed sample was visually and qualitatively assessed.

3.3 Design of Experiments

For the Design of Experiments (DoE) analysis, five levels of performance of the deinking process were assigned. The classification used for the deinking performance is shown in Table 2.

Table 2. Classification used for the deinking performance.

Classification	Description
No deinking (1)	No evident effects of the surfactant agent
Poorly deinked (2)	Low or no effect of the surfactant agent
Lightly deinked (3)	Slight and visible effects of the surfactant agent
Mostly deinked (4)	Evident effects of the surfactant agent, but not full deinking
Fully deinked (5)	Full deinking achieved

Table 3. Testing conditions for the DoE analysis.

StdOrder	Surfactant concentration [%]	Bath temperature [°C]	Bath time [s]	Brush [iteration]
1	2,5	25	30	1
2	5	25	30	5
3	2,5	40	30	5
4	5	40	30	1
5	2,5	25	60	5
6	5	25	60	1
7	2,5	40	60	1
8	5	40	60	5
9	2,5	25	30	5
10	5	25	30	1

(continued)

Table 3. (continued)

StdOrder	Surfactant concentration [%]	Bath temperature [°C]	Bath time [s]	Brush [iteration]
11	2,5	40	30	1
12	5	40	30	5
13	2,5	25	60	1
14	5	25	60	5
15	2,5	40	60	1
16	5	40	60	5

The factorial design analysis created results on 24 condition tests to use on the Minitab software [22]. With performance as the response variable, the expected output was related to the increase in performance of the chemical reaction. To such end, four factors were tested, namely the bath temperature (25 °C and 40 °C), surfactant concentration (5% against 2.5%), bath time (30 s against 1 min) and impact of brushing (once to five times), as listed in Table 3.

4 Results and Discussion

Deinking relates to removing the printing layers on the plastic film. The strips were treated with 2.5% and 5% of surfactant solutions at approximately pH 8 and magnetically stirred. For the set of analyses carried out, the deinking level of the 16 samples was established and classified according to the criteria presented in Table 2.

Figure 1.a) shows a sample where no evidence of deinking was observed due to the action of the surfactant, while in the sample Fig. 1.b) it was possible to identify a reduced effect of the surfactant. Figure 1.c) depicts visible effects of deinking, but not too effective. Finally, Figs. 1.d) and 1.e) show the best deinking results, particularly those of Fig. 1.e), where complete deinking took place.

Table 4 shows the deinking performance results obtained for each testing procedure, ordered from the best deinking performance to the less performing condition.

From Table 4, it is possible to observe that the bath temperature is the most critical factor in the effectiveness of the deinking process. Figure 2 plots the main effects of surfactant concentration, bath temperature, bath time and brushing iterations for the deinking performance.

The main effects on the impact of deinking performance are the bath temperature and the surfactant concentration, as can be observed in Fig. 2. When the bath temperature is 40 °C, the deinking performance is significantly higher when compared to the same results for a temperature of 25 °C. Following the same trend, the deinking performance is significantly improved for the higher surfactant concentration. On what refers to the bath time and brushing iterations, the deinking performance is less affected but follows the same trend as the other factors for the higher values.

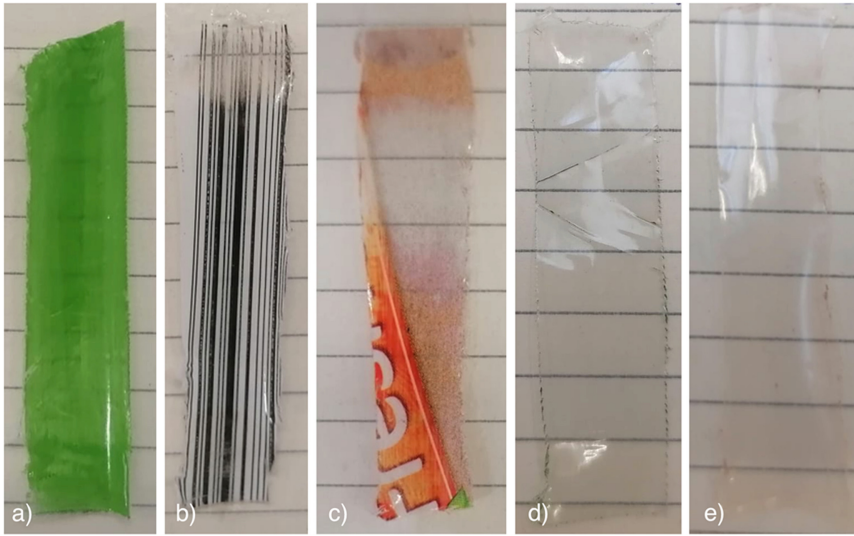


Fig. 1. Classification of the processed samples.

Table 4. Deinking performance results.

StdOrder	Surfactant concentration [%]	Bath temperature [°C]	Bath time [s]	Brush [iterations]	Deinking performance
4	5	40	30	1	5
8	5	40	60	5	5
12	5	40	30	5	5
16	5	40	60	5	5
3	2,5	40	30	5	4
7	2,5	40	60	1	4
11	2,5	40	30	1	4
15	2,5	40	60	1	4
6	5	25	60	1	3
14	5	25	60	5	3
2	5	25	30	5	2
5	2,5	25	60	5	2
10	5	25	30	1	2
1	2,5	25	30	1	1
9	2,5	25	30	5	1
13	2,5	25	60	1	1

On what concerns the sustainability of the deinking process, a detailed analysis of the entire lifecycle of all materials involved would be required. For the current results,

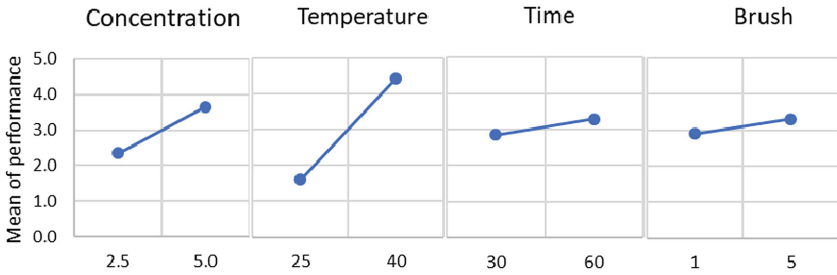


Fig. 2. Main effects plot for performance (fitted means).

however, it is important to note that the most relevant factors for the deinking process are the same factors that need to be balanced.

A higher bath temperature requires additional energy when compared to the lower temperature condition. Considering that such increased demand for electric energy may have different economic and environmental impacts, namely, regarding alternative fossil fuel or renewable sources, further analysis of the life cycle impacts is required.

When considering the effect of the surfactant concentration, the use of an eco-friendly surfactant may be beneficial to the process not only from the standpoint of enhancing the deinking process but also from the sustainability perspective. Thus, the increased use of an eco-friendly surfactant may have a lower environmental impact when compared to the alternative solution of increasing the bath temperature to 40 °C. Nevertheless, the energy required to produce the surfactant agent is not considered in this case study. This supports the need for a complete life cycle assessment of the proposed deinking process as further research.

5 Conclusion

The current research case study focused on the process of ink removal on plastic films printed by flexography. Considering that the printed layers are some of the main challenges to address when discussing the circularity of recycling such coated plastics, the use of bio-surfactants was proposed to lower the environmental impacts on its deinking process.

Dedicated laboratory deinking procedures were undertaken with transparent polyethylene films printed by flexography with different conditions. Preliminary results showed the dedicated experimental ink removal procedure using bio-based surfactants to be effective in the removal of the coated layers on post-industrial waste films.

A design of experiments analysis was conducted with five levels of performance of the deinking process. To such end, four factors were tested, namely the bath temperature, surfactant concentration, bath time and the impact of brushing. The computed results showed the bath temperature and the surfactant concentration to have the highest impacts on the deinking performance.

As the main findings, it was highlighted that the higher bath temperature and the higher surfactant concentration were beneficial in maximizing the results of the deinking process. However, to discuss the environmental sustainability aspects of the proposed

deinking process using bio-based surfactants, future research analyzing the life cycle assessment of the process is required.

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References

1. Plastics Europe: Plastics-the Facts 2021 An analysis of European plastics production, demand and waste data (2022). <https://plasticseurope.org/>. Accessed 22 Apr 2022
2. Fogt Jacobsen, L., Pedersen, S., Thøgersen, J.: Drivers of and barriers to consumers' plastic packaging waste avoidance and recycling – a systematic literature review. *Waste Manage.* **141**, 63–78 (2022). <https://doi.org/10.1016/j.wasman.2022.01.021>
3. Chotipong, A., Scamehorn, J.F., Rirkosomboon, T., et al.: Removal of solvent-based ink from printed surface of high-density polyethylene bottles by alkyltrimethylammonium bromides: Effects of pH, temperature, and salinity. *Colloids Surf., A* **297**, 163–171 (2007). <https://doi.org/10.1016/j.colsurfa.2006.10.043>
4. Gecol, H., Scamehorn, J.F., Christian, S.D., Riddell, F.E.: Use of surfactants to remove solvent-based inks from plastic films. *Colloid Polym. Sci.* **281**, 1172–1177 (2003). <https://doi.org/10.1007/s00396-003-0891-4>
5. Hopewell, J., Dvorak, R., Kosior, E.: Plastics recycling: challenges and opportunities. *Philos. Trans. R. Soc. B: Biol. Sci.* **364**, 2115–2126 (2009)
6. Kane, S., van Roijen, E., Ryan, C., Miller, S.: Reducing the environmental impacts of plastics while increasing strength: biochar fillers in biodegradable, recycled, and fossil-fuel derived plastics. *Compos. Part C: Open Access* **8**, 100253 (2022). <https://doi.org/10.1016/j.jcomc.2022.100253>
7. Hou, P., Xu, Y., Taiebat, M., et al.: Life cycle assessment of end-of-life treatments for plastic film waste. *J. Clean. Prod.* **201**, 1052–1060 (2018). <https://doi.org/10.1016/j.jclepro.2018.07.278>
8. Horodytska, O., Kiritsis, D., Fullana, A.: Upcycling of printed plastic films: LCA analysis and effects on the circular economy. *J. Clean. Prod.* **268**, 122138 (2020). <https://doi.org/10.1016/j.jclepro.2020.122138>
9. Gecol, H., Scamehorn, J.F., Christian, S.D., et al.: Use of surfactants to remove water based inks from plastic films. *Colloids Surf. A* **189**, 55–64 (2001). [https://doi.org/10.1016/S0927-7757\(01\)00591-X](https://doi.org/10.1016/S0927-7757(01)00591-X)
10. Yousef, S., Muumladze, T., Tatariants, M., et al.: Cleaner and profitable industrial technology for full recovery of metallic and non-metallic fraction of waste pharmaceutical blisters using switchable hydrophilicity solvents. *J. Clean. Prod.* **197**, 379–392 (2018). <https://doi.org/10.1016/j.jclepro.2018.06.154>
11. World surfactants market outlook to 2023. Focus on Surfactants 3 (2023). <https://doi.org/10.1016/j.fos.2020.04.011>
12. Farias, C.B.B., Almeida, F.C.G., Silva, I.A., et al.: Production of green surfactants: Market prospects. *Electron. J. Biotechnol.* **51**, 28–39 (2021). <https://doi.org/10.1016/j.ejbt.2021.02.002>
13. Müller, M.M., Kügler, J.H., Henkel, M., et al.: Rhamnolipids—Next generation surfactants? *J. Biotechnol.* **162**, 366–380 (2012). <https://doi.org/10.1016/j.jbiotec.2012.05.022>

14. Doshi, B., Sillanpää, M., Kalliola, S.: A review of bio-based materials for oil spill treatment. *Water Res.* **135**, 262–277 (2018). <https://doi.org/10.1016/j.watres.2018.02.034>
15. Liyana Ismail, N., Shahrudin, S., Othman, J.: Overview of bio-based surfactant: recent development, industrial challenge, and future outlook. In: *Surfactants [Working Title]*. IntechOpen (2022)
16. ISO/DIS 21680. <https://www.iso.org/obp/ui/fr/#iso:std:iso:21680:dis:ed-1:v1:en>. Accessed 22 Apr 2022
17. CEN/TC 276: EN 17035:2021 Surface active agents - Bio-based surfactants - Requirements and test methods. European Commission of Standardization (2021)
18. Piloat, A.: Method and apparatus for recycling printed plastic films. EP20030356181 (2004)
19. Meccanica, G.: Cleaning system for the removal of printing ink from flexible plastic films (2016)
20. Cameotra, S.S., Makkar, R.S., Kaur, J., Mektha, S.K.: Synthesis of biosurfactants and their advantages to microorganisms and mankind. In: Sen, R. (ed.) *Biosurfactants*, pp. 261–280. Springer, New York (2010). https://doi.org/10.1007/978-1-4419-5979-9_20
21. Ye, X., Wu, Z., Wang, M., et al.: Example of removing printing ink from plastic surface using quaternary ammonium-modified waste cooking oil. *Environ. Technol.* 1–12 (2021). <https://doi.org/10.1080/09593330.2021.1983026>
22. Minitab Statistical Software. <https://www.minitab.com>. Accessed 22 Apr 2022



Evaluation of the Possibility to Use By-Products of Gasification and Carbonization from Polymeric Residues and Biomass

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Abstract. The search for strategies that contribute to a circular economy, based on the valorization of by-products of the most diverse industries and processes, is one of the main objectives nowadays. This study aims to evaluate the possibility of the by-products valorization, resulting from gasification and carbonization of polymeric residues and biomass of natural origin, through their application in adsorption processes. The selected residues and carbon by-products resulting from the thermochemical conversion by gasification and carbonization processes, after their physical and chemical characterization, were evaluated intending to find if it was possible to improve their structural and chemical properties to apply them in adsorption processes. The characterization of the materials and samples prepared in this work involved a variety of analytical techniques as Thermogravimetric analysis (TGA), Polarized attenuated Fourier transform infrared spectroscopy (FTIR-ATR), X-Ray fluorescence (XRF) and Nitrogen Adsorption at 77K. It was possible to see that the material has between 40 and 50% of volatile matter and when carbonized these values are between 5 and 10%. Regarding the higher calorific value, the carbonized materials had an increase of approximately 9% in relation to the material without pre-treatment. It was verified that the apparent surface area (BET) of these chars was between 100 and 300 m²g⁻¹.

Keywords: Circular economy · Adsorption · Carbonization · Biochars

1 Introduction

The search for strategies that contribute to a circular economy, based on the valorization of by-products derivate from the most diverse industries and processes, is one of the main objectives nowadays. For this reason, it is important to try to use residues from different sources and give them different uses.

Solid waste management is a global problem. Has a high cost, and worldwide is around 2.01 billion tons of municipal solid waste per year (Kaza et al. 2018). In the

future, waste is expected to grow worldwide to 3.40 billion tons by the year 2050. At the Global level, most waste is currently dumped or disposed of in landfill (Kaza et al. 2018).

The total production of municipal solid waste in Portugal was approximately 5278502 tons in 2020, corresponding to an annual capitation of 512.6 kg/(habitant/year), a daily production of solid waste of 1.4 kg per habitant (Environment State Portal 2022). The most employed strategies for energy recovery from waste are refuse incineration or raw waste processing. From the raw waste processing it is obtained a refuse derived fuel (RDF) (Nobre et al. 2019). These residues are passive to be valorized by flow chemical technology, pyrolysis and gasification (Abdel-Shafy and Mansour 2018). There are another type of residues generated by agricultural activity, like residues from Olive tree pruning (OTP), they are organic waste materials and can be valorized to produce green fuels and value-added products through thermochemical conversion processes (Okolie et al. 2022). Lignocellulosic biomass is characterized by being a heterogeneous material in composition, hygroscopic nature, high moisture content low calorific value and low bulk density (Sarker et al. 2021). Biomass is composed normally by 40–50% cellulose, 25–35% hemicellulose, 15–20% lignin (Ginni et al. 2021).

Usually, the energy recovery of agricultural residues can be done by non-oxidative and oxidative thermochemical processes such as combustion, gasification and pyrolysis (Ginni et al. 2021).

This work aims to use by products and transformed them in added value products that can be used to other ends, such as adsorbents of pollutants, filters, and others (Mourão et al. 2006). The full characterization of the raw materials and selected samples will be presented and discussed in order to confirm the potential of this strategy for the production of adsorbent materials.

2 Experimental

2.1 Samples

The raw biomass used for this study were CMC and OTP. The OTP, Fig. 1, is a lignocellulosic biomass well studied, and it comes from olive tree branches. The CMC biomass is showed in Fig. 2 and it's characterized for being from pine tree and a has in the composition really small part of plastic residues. This CMC biomass originates from the recycling of furniture and residues from the manufacturing process, it is supplied by a Portuguese company called CMC Biomassa. The reception of the samples was made at BioBip Energy, and the samples are described above.



Fig. 1. Aspect of the samples used for this work. OTP raw, Carbonized OTP (100%) and Carbonized OTP+RDF (90–10%).



Fig. 2. Aspect of the samples used for this work. CMC raw, Carbonized CMC (100%) and Carbonized CMC+RDF (90–10%).

2.2 Methods

2.2.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed by a STA6000 analyzer (PerkinElmer), 30 °C and 995 °C in steps of 10 °C /min. An initial ramp segment of 30 °C/min was used to reach the selected temperature, chosen by the authors to yield highly carbonized biochars. The TGA analysis was purged without gas flow, the analysis was performed with a mass of sample around 5 mg.

2.2.2 Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectra were collected using a Thermo Scientific model Nicolet iS10 ATR SMART iTR in transmission mode from 500 to 4000 cm^{-1} with a resolution of 1 cm^{-1} . For the more heterogeneous samples, 3 scans were collected to ensure the accuracy of the sample. For the other samples was collected just on sample.

2.2.3 Nitrogen Adsorption at 77K

Brunauer-Emmett-Teller (BET) specific surface area analysis was performed using *Micrometrics*, model ASAP 2020. The samples were analyzed under nitrogen atmosphere (adsorption-desorption isotherms at 77 K) in a volumetric working device.

2.2.4 Calorimetric Analysis

For the Calorimetric analysis, the procedure used is based on ASTM E711-87 standards and using a digital heat pump, model IKA C2000. Samples were previously dried and homogenized, and weighed about $0.5 \pm 0.1\text{g}$. This Calorimetric analysis give the PCS (higher calorific value) of the material.

2.2.5 X-Ray Fluorescence (XRF) Analysis

X-Ray fluorescence analysis was performed at a Thermo Scientific Niton XRF Analyzer. This analysis was performed with a weighted media of three analyses.

3 Results and Discussions

The main objective of this work is to evaluate the possibility of the by-products valorization, resulting from gasification and carbonization of polymeric residues and lignocellulosic biomass, through their application in adsorption processes. The obtained samples of all the raw material, the carbonized raw materials and selected mixtures were investigated by a set of characterization techniques.

3.1 TGA Analysis

TGA analysis is a method used to determinate the sample weight changes in function of temperature (Abdel daiem et al. 2021). DTG is the name given to the derivate of the TGA analysis. In this work the TGA/DTG analysis was implemented from 30 °C up to 950 °C at a step of 10 °C per minute.

In the Fig. 3 and Fig. 4 it is possible to see that both biomasses have a low humidity content, and that the CMC raw material has a much higher ash content that the OTP raw.

For the raw biomasses, the first changes on the curve where derived from the drying of the biomasses materials and also some moisture and certain volatile compounds are eliminated, normally from the initial temperature until 180 °C (Garcia-Maraver et al. 2013).

When considered lignocellulosic biomasses, the degradation temperature of the hemicellulose and lignin is lower them the found in the cellulose (Garcia-Maraver et al. 2013). It is also important to point out that a material with a high percentage of ashes and impurities have lower initial degradation temperatures (Garcia-Maraver et al. 2013).

Hemicellulosic component began to break down at temperatures above the 180 °C (Garcia-Maraver et al. 2013). The maximum weight was verified in the region of fast combustion approximately between 280 °C and 480 °C. The profiles of the thermogravimetric curves show that the CMC biomass presents an initial inertia to transformation, reaction and degradation as a function of temperature, higher than that of the OTP, which is even more evident in the upper temperature range (around 400 °C).

The thermal behavior of the RDFs, Fig. 5, is clearly different, which is explained by the nature and composition of this material. We are in the presence of a material composed of a mixture of constituents of very different natures (inorganic and organic), namely plastics, rubber, aluminum, food waste, wood, inerts and others, which determines a distinct thermogravimetric profile, with very distinct reactivity and mass loss. Reactivity and mass variation occur with particular incidence in the range between 250 and 550 °C, and the final residual mass reaches very high values, around 50%.

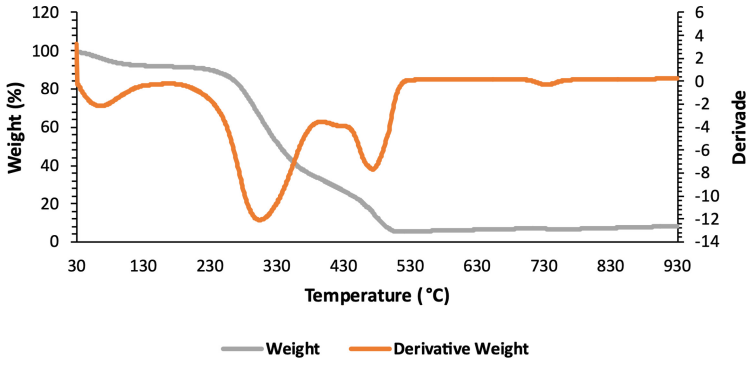


Fig. 3. Graphic of the TGA analysis for the sample OTP raw.

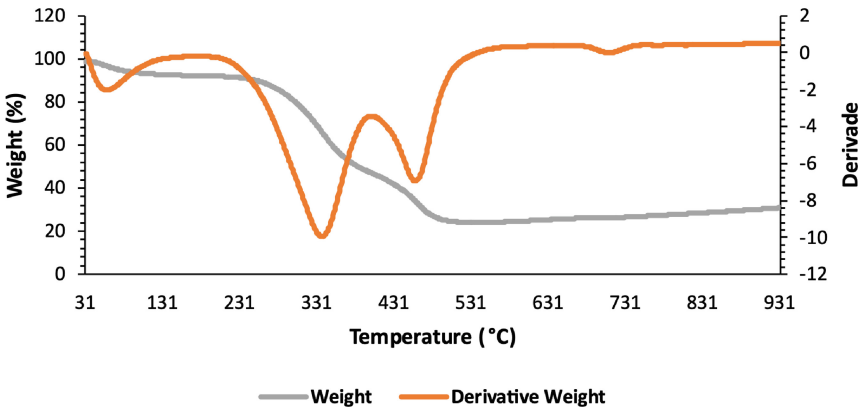


Fig. 4. Graphic of the TGA analysis for the sample CMC raw.

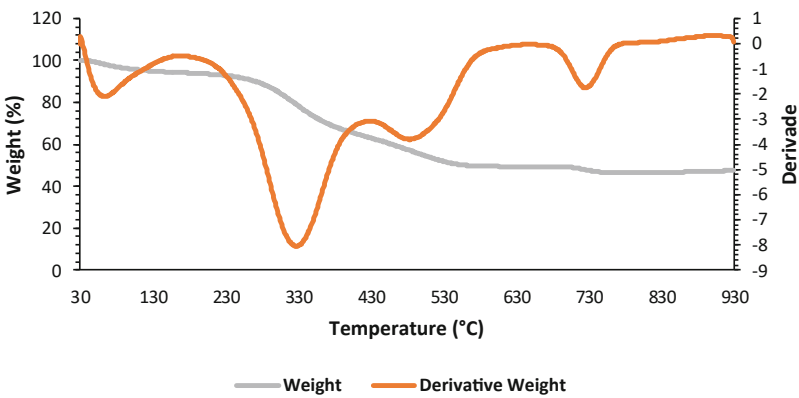


Fig. 5. Graphic of the TGA analysis for the sample RDF raw.

In the Fig. 6 and Fig. 7 it is possible to see that both carbonized biomasses have a low humidity content (possible from atmospheric air), and a small amount of volatile matter and a really high percentage of fixed carbon. This behavior is typical of carbonized biomasses and its present for both biomasses, CMC and OTP raw.

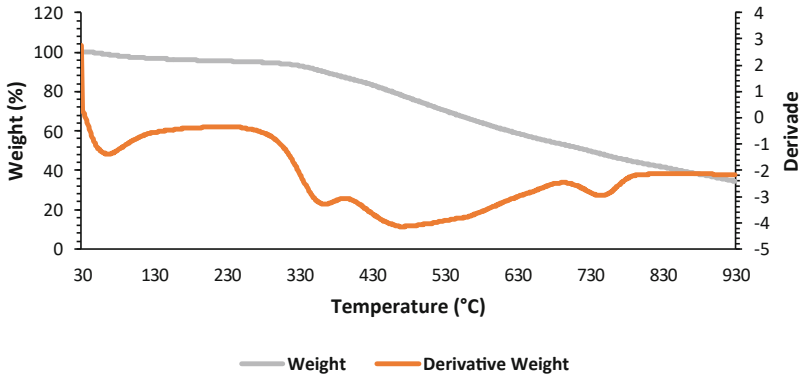


Fig. 6. Graphic of the TGA analysis for the sample Carbonized CMC (100%).

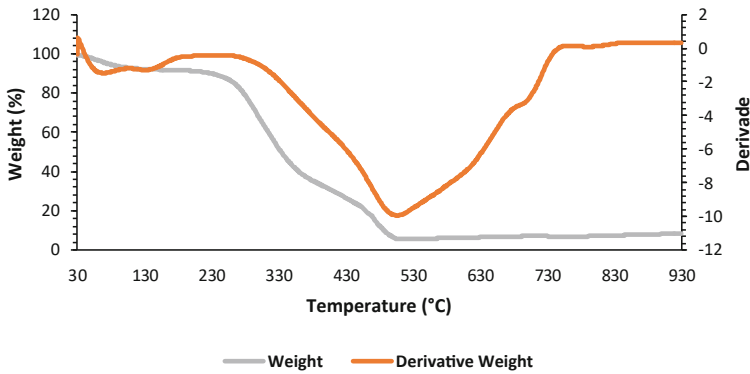


Fig. 7. Graphic of the TGA analysis for the sample Carbonized OTP (100%).

For the mixtures presented in the Fig. 8 and Fig. 9 they have a similar behavior than the carbonized biomasses.

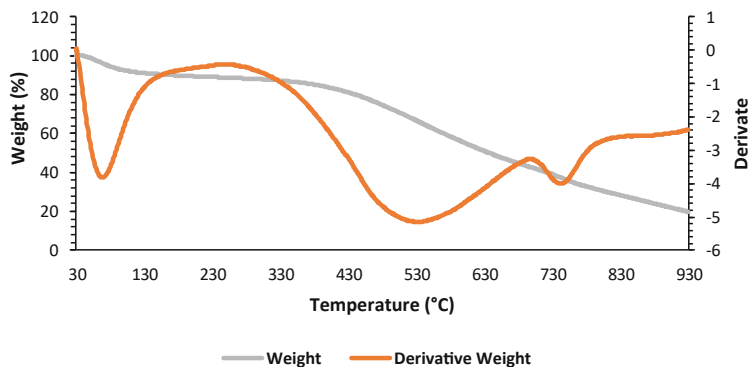


Fig. 8. Graphic of the TGA analysis for the sample Carbonized CMC+RDF (90–10%).

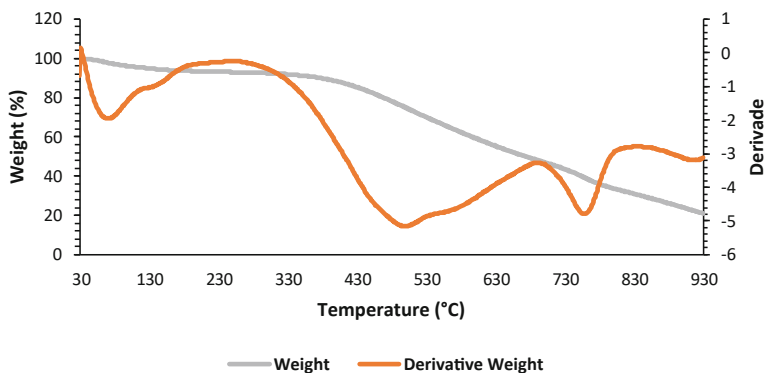


Fig. 9. Graphic of the TGA analysis for the sample Carbonized OTP+RDF (90–10%).

3.2 FTIR Spectroscopy

FTIR spectroscopy is used to identifying the functional groups presents in the samples, the type of chemical bonds, namely the presence of specific atoms, like oxygen, sulfur, chlorine or other heteroatoms, in the samples that could play an important role on the adsorption process(Pijović et al. 2022).

The Fig. 10, Fig. 11 and Fig. 12 referred to the FTIR analysis of the samples. It is possible to see that there are not relatively big differences between the carbonized samples (just biomass and mixtures). For de RDF there is a really big difference between the raw material and the carbonized, the large majority of the functional groups present on the raw material are not in the carbonized material. This feature could be explained by the strong impact that the thermal treatment have on this composed material, leading to a more poor material from the chemical pint of view.

According to Maneerung et al. (2016) the principal functional groups found at the samples are the bands located between $3200\text{--}3500\text{ cm}^{-1}$ which can possible be attributed to the O–H stretching of the hydroxyl groups. The bands seen at approximately 2928 and 2398 cm^{-1} can possible be assigned to the C–H stretching of the methyl groups. The bands that are presented at approximately 1066 cm^{-1} can possible be assigned to the

C–O, and the bands between $1610\text{--}1700\text{ cm}^{-1}$ are from the groups C=O stretching of the carboxyl groups. At around 900 cm^{-1} it is possible to see the vibration of aromatic compounds (Manerung et al. 2016).

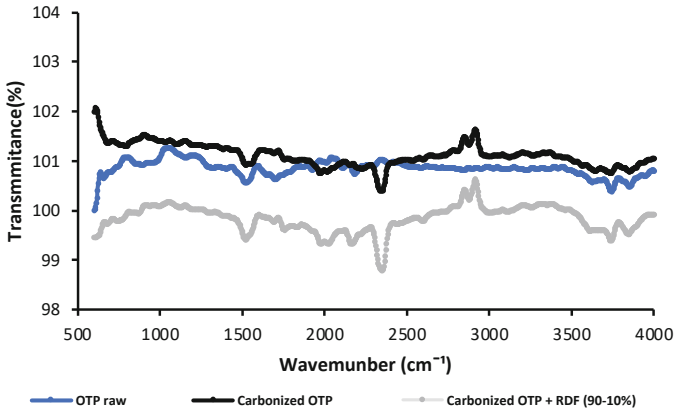


Fig. 10. Graphic of FTIR analysis for the sample OTP raw, Carbonized OTP and Carbonized OTP+RDF (90–10%).

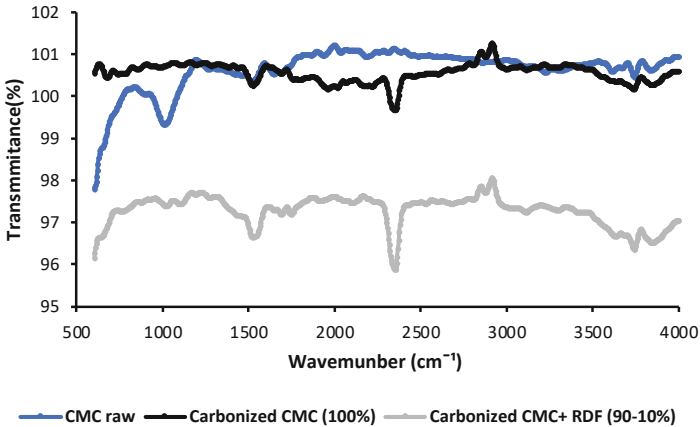


Fig. 11. Graphic of FTIR analysis for the sample CMC raw, Carbonized CMC and Carbonized CMC+RDF (90–10%).

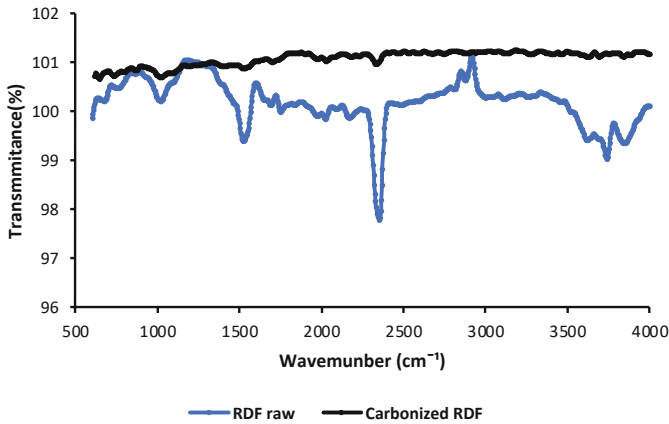


Fig. 12. Graphic of FTIR analysis for the sample RDF raw and Carbonized RDF.

3.3 Nitrogen Adsorption at 77K

The specific surface area of samples was calculated according to the Brunauer-Emmett-Teller (BET) method. It was used the linear part of the nitrogen adsorption isotherms for each sample (Pijović et al. 2022).

In Table 1 are showed the values obtain for the apparent surface area (BET) of the carbonized materials. The values obtain for these samples are approximately between 180 and 215 m^2/g .

It is reported by Maneereung et al. (2016) that on char of mesquite wood chips, similar to the biomasses on study, the surface area (BET) of the char was 172.24 m^2/g . For the sample CMC we can observe that the incorporation of the RDF leads to a decrease on the surface area (BET) For the sample OTP, it's the contrary, the incorporation of the RDF material increases the BET Surface Area in 10 m^2/g . Although the variations observed are slight, this distinct behavior can be explained by the different nature of the biomass precursors, which will lead to the formation of lightly different RDF-Biomass interactions. This interpretation can be confirmed by FTIR analysis, which highlights this slight difference of chemical nature, and now also a structural variation with measurable consequences by BET analysis.

Table 1. Values obtained for BET analysis for the carbonized samples.

Sample	S_{BET} (m^2/g)
Carbonized CMC (100%)	211
Carbonized CMC + RDF (90–10%)	182
Carbonized OTP (100%)	199
Carbonized OTP + RDF (90–10%)	210

3.4 Calorimetric Analysis

In Table 2 are showed the results of PCI for all the samples in study. For the carbonized materials the PCI increases. The PCI reported by Fawzy et al. (2022) for the biomass of OTP raw is 17.61 MJ.kg^{-1} . In this study the value found was $17,65 \text{ MJ.kg}^{-1}$. Thereby, the values are suchlike. The CMC biomass is also comparable with this value. The carbonized material has a higher PCI, because has a more concentrated carbon yield.

Table 2. Higher calorific value (PCI) values obtained for each of the studied samples.

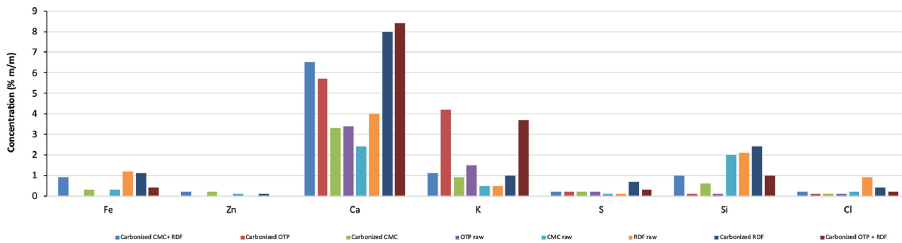
Sample	HHV (MJ/kg)
CMC raw	16,387
OTP raw	17,650
RDF raw	18,530
Carbonized CMC (100%)	24,588
Carbonized OTP (100%)	27,520
Carbonized RDF (100%)	29,136
Carbonized CMC+RDF (90–10%)	19,240
Carbonized OTP+RDF (90–10%)	26,910

3.4.1 XRF Analysis

When we talk about thermochemical processes it is very important to considerate the Cl content of the material, since if the concentration of Cl is high it can bring serious problems as the deterioration of the equipment's and formation of toxic gasses. In Table 3 it is displayed the Cl content of itch sample. The RDF is the sample that has the highest Cl content. For these samples the carbonization decreases the Cl content in the samples. For the rest of the representative elements, are showed in the Fig. 13, this graphic tells that the elements in higher concentrations are the Ca and K, and the elements with lower concentration are the S and Zn. The percentage of chlorine present in the biochars tends to increase with increasing when carbonized the material, due to the loss of mass of the sample and the devolatilization of the chlorine that is deposited on the sample surface (Mota-Panizio et al. 2022). In this case, it doesn't happen.

Table 3. Cl content values obtained for each of the studied samples.

Sample	Cl content (%m/m)
CMC raw	0,36
OTP raw	0,23
RDF raw	0,85
Carbonized CMC (100%)	0,22
Carbonized OTP (100%)	0,12
Carbonized RDF (100%)	0,27
Carbonized CMC + RDF (90–10%)	0,16
Carbonized OTP + RDF (90–10%)	0,15

**Fig. 13.** Representative elements of the mineral composition of the material.

4 Conclusions

The production of carbon-neutral materials from renewable resources, as the ones showed, is playing an increasingly important role in gradually replacing traditional fossil processes and has received extensive attention from the academic field.

The CMC biomass has more ash content than the biomass OTP. With the FTIR analysis it is proved that there are changes in the functional groups of the biomass when added the RDF, but it's considered that the changes are not that significant. In terms of BET surface area analysis, the CMC biomass shows a lower BET surface area when add the RDF. For the OTP it's the contrary, the BET surface area increases when add RDF. The PCI and the Cl content of the samples lead us to believe that these materials are adequate for thermochemical valorization. This is a preliminary study, that aims to characterize the raw biomass for future works that will be performed with this chars. With the results obtained in this study the authors consider these materials have potential for activation and future studies.



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References

- Abdel Daiem, M.M., Rashad, A.M., Said, N., Abdel-Gawwad, H.A.: An initial study about the effect of activated carbon nano-sheets from residual biomass of olive trees pellets on the properties of alkali-activated slag pastes. *Journal of Building Engineering* **44**(May), 102661 (2021). <https://doi.org/10.1016/j.job.2021.102661>
- Abdel-Shafy, H.I., Mansour, M.S.M.: Solid waste issue: sources, composition, disposal, recycling, and valorization. *Egypt. J. Pet.* **27**(4), 1275–1290 (2018). <https://doi.org/10.1016/j.ejpe.2018.07.003>
- Fawzy, S., Osman, A.I., Farrell, C., Al-Muhtaseb, A.H., Harrison, J., Rooney, D.W.: Kinetic modelling for pyrolytic degradation of olive tree pruning residues with predictions under various heating configurations. *Process Saf. Environ. Prot.* **161**, 221–230 (2022). <https://doi.org/10.1016/j.psep.2022.03.042>
- García-Maraver, A., Salvachúa, D., Martínez, M.J., Díaz, L.F., Zamorano, M.: Analysis of the relation between the cellulose, hemicellulose and lignin content and the thermal behavior of residual biomass from olive trees. *Waste Manage.* **33**(11), 2245–2249 (2013). <https://doi.org/10.1016/j.wasman.2013.07.010>
- Ginni, G., et al.: Valorization of agricultural residues: different biorefinery routes. *J. Environ. Chem. Eng.* **9**(4), 105435 (2021). <https://doi.org/10.1016/j.jece.2021.105435>
- Kaza, S., Yao, L., Tata-Bhanda, P., Van Woerden, F.: What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050 (Issue 1) (2018). <https://doi.org/10.16309/j.cnki.issn.1007-1776.2003.03.004>
- Maneering, T., Liew, J., Dai, Y., Kawi, S., Chong, C., Wang, C.H.: Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: kinetics, isotherms and thermodynamic studies. *Biores. Technol.* **200**, 350–359 (2016). <https://doi.org/10.1016/j.biortech.2015.10.047>
- Mota-Panizio, R., Hermoso-Orzáez, M.J., Carmo-Calado, L., Calado, H., Gonçalves, M.M., Brito, P.: Co-carbonization of a mixture of waste insulation electric cables (WIEC) and lignocellulosic waste, for the removal of chlorine: biochar properties and their behaviors. *Fuel*, **320**(March) (2022). <https://doi.org/10.1016/j.fuel.2022.123932>
- Mourão, P.A.M., Carrott, P.J.M., Ribeiro Carrott, M.M.L.: Application of different equations to adsorption isotherms of phenolic compounds on activated carbons prepared from cork. *Carbon* **44**(12), 2422–2429 (2006). <https://doi.org/10.1016/j.carbon.2006.05.015>
- Nobre, C., Vilarinho, C., Alves, O., Mendes, B., Gonçalves, M.: Upgrading of refuse derived fuel through torrefaction and carbonization: evaluation of RDF char fuel properties. *Energy* **181**, 66–76 (2019). <https://doi.org/10.1016/j.energy.2019.05.105>
- Okolie, J.A., et al.: Waste biomass valorization for the production of biofuels and value-added products: a comprehensive review of thermochemical, biological and integrated processes. *Process Saf. Environ. Prot.* **159**, 323–344 (2022). <https://doi.org/10.1016/j.psep.2021.12.049>
- Pijović, M., et al.: Simple and effective one-step production of high-quality mesoporous pyrolytic char from waste tires: Rhodamine B adsorption kinetics and density functional theory (DFT) study. *Diamond Relat. Mater.* **121**(2021) (2022). <https://doi.org/10.1016/j.diamond.2021.108768>
- PORDATA: Resíduos urbanos recolhidos selectivamente ou reciclados (%) (2022). [https://www.pordata.pt/Portugal/Resíduos+urbanos+recolhidos+selectivamente+ou+reciclados+\(percentagem\)-1104](https://www.pordata.pt/Portugal/Resíduos+urbanos+recolhidos+selectivamente+ou+reciclados+(percentagem)-1104)
- Sarker, T.R., Nanda, S., Dalai, A.K., Meda, V.: A review of torrefaction technology for upgrading lignocellulosic biomass to solid biofuels. *BioEnergy Res.* **14**(2), 645–669 (2021). <https://doi.org/10.1007/s12155-020-10236-2>



Circular Economy of Water: A Review of Scientific Production

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Abstract. The general aim of the research was to analyse the scientific production on the circular economy of water in the Web of Science database. The systematic and integrative review used the Methodi Ordinatio, which made it possible to identify the most relevant articles on the circular economy of water. The main findings were the identification of 38 articles on the circular economy of water, in which the years 2018 and 2020 were the years with the most publications. The contexts already studied demonstrated that the circular economy is related to assessing the life cycle, the techniques related to the reuse and recovery of water, education models and strategic issues. The areas surveyed were mainly associated with the public area, tourism, entrepreneurship and manufacturing. It is essential to emphasise the importance of research related to water since the concern with this resource has been observed. The discussions are far from being exhausted; therefore, a proposal for a future agenda has been presented, indicating the direction for future research about the theme.

Keyword: Sustainability · Circular economy · Water

1 Introduction

Freshwater consumption has increased sharply since 1950. Conversely, since 2000, consumption has remained stable. The countries that most withdraw freshwater are India, China and the United States. The biggest water consumers are agriculture, around 70%; industries, about 19%; and cities, about 11% [1].

The countries that consume the most water in their industrial operations are the United States, around 300 billion m³ per year; China, around 140 billion m³; Russia, about 40 billion m³ and Brazil, about 12 billion m³ per year. All this water consumption is seen as worrying since the risk of water scarcity may occur [1]. However, industries are seen as drivers of economic development in countries. On the other hand, many of these industries need to consume a significant volume of water in their production systems [2].

Because of this concern about water consumption on the planet, which may face a water deficit by 2030 [3, 4], there has been an increase in concern about the possible lack of water and, consequently, seeking to reduce consumption. However, this practice

alone may not be enough, and therefore, it is necessary to seek other ways to meet the total water demand. One way that has been drawing attention in the circular economy is the reuse of water [5]. Mannina et al. [6] reinforce that the circular economy of water should direct attention to aspects related to technology, social and economic issues and legislative aspects.

Due to the concern presented in the 2030 Agenda, which proposes the 17 sustainable development goals (SDGs), which include SDG 6 - drinking water and sanitation, which values the efficient use of water and reuse technology and the SDG 9 – industry, innovation and infrastructure which seeks to make industries more sustainable and seeking to adopt cleaner production processes [7].

Faced with a possible water scarcity scenario, studies related to the consumption or reuse of water is necessary. Since it is necessary for the survival of individuals, several industries depend on water and have a prominent role in sustainable development [3, 8].

In this sense, the general aim of the research was to analyse the scientific production on the circular economy of water in the Web of Science database. The specific objectives are: (i) to identify the articles that relate the circular economy to water; (ii) identify the most relevant journals on the subject; (iii) identify the ten most relevant articles on the subject; (iv) to analyse in an integrative way the articles identified on the subject; (v) propose an agenda for future studies.

The article is organised as follows: in this first section, the importance of the theme is presented together with the proposed aims; in the second section, the methodological course of the research is presented; the third section contains the results and discussions and; finally, the last section presents the final considerations together with the limitations of the research.

2 Methodology

The present research is a systematic literature review; the selected database was the Web of Science; Methodi Ordinatio was used to identify the most relevant articles on the subject; to analyse the results, a quantitative approach was used, and integrative analysis of the ten most relevant articles on the subject under study was carried out.

The research is a systematic review as it aims to identify and recognise research on a particular theme. In addition to methodological rigidity, it aims to answer a research question and synthesises the identified works [9–11]. It is necessary to choose a database to carry out a systematic review. The Web of Science was chosen in the present research, as it is among the most reputable databases [12].

For the research to have methodological rigidity, the Methodi Ordinatio was used, which is considered a systematic review methodology that aims to direct the research, assist in data collection and classify articles with the help of JabRef, Mendeley and Microsoft Excel software [13].

Methodi Ordinatio has the InOrdinatio index, which aims to identify the most relevant articles on a given topic; this index takes into account the impact factor of the journal, in the present research, it takes into account the JCR; the year of publication of the article and, finally, the number of citations that the article has on Google Scholar [14].

Entering the searches for articles on the research topic, which took place in May 2021, the Web of Science database was accessed, and the following strings ‘circular economy’ AND ‘water’ were used, considering only the titles of the articles. In the first round of searches, 49 documents were identified. The ‘Article’ filter was applied, identifying 39 articles. The next step was to analyse all the titles of the articles, which identified and excluded a duplicate article. Finally, 38 articles were considered, and the InOrdinatio index was calculated to identify the ten most relevant articles on the subject under study.

After identifying the twelve most relevant articles, two articles were excluded from the final analysis because titles, abstracts and keywords, were not aligned with the focus of the present research. It was possible to identify the history of publications per year by analysing the results obtained. It was possible to identify the most relevant journals on the subject, generating an index that divides the number of total citations by the number of articles published in the journal. The titles and keywords of the ten articles were analysed using Word Cloud, which emphasises the most repeated words.

In order to carry out a deeper analysis of the most relevant articles, the integrative analysis was used, which seeks to present a synthesis of the knowledge presented in the analysed articles [15]; and, finally, this research proposes an agenda for future research based on the ten most relevant articles on the subject.

Table 1 presents the general and specific aims of the research and the methodological procedures in a summarised way used to achieve the aims proposed in the research.

Table 1. Summary of methodological procedures adopted.

General aim	Specific aims	Methodological procedures
To analyse the scientific production on the circular economy of water in the Web of Science database	(i) identify the articles that relate the circular economy to water	Database: Web of Science and Methodi Ordinatio
	(ii) identify the most relevant journals on the subject	Descriptive Statistics and Citation Index by the number of articles
	(iii) identify the ten most relevant articles on the subject	InOrdinatio Index
	(iv) to analyse in an integrative way the articles identified on the subject	Integrative analysis of the ten most relevant articles
	(v) propose an agenda for future studies	

After presenting the methodological procedures used in this research, the following section presents the research results and discussions.

3 Analysis and Discussion of Results

Entering the analysis of the results obtained, Fig. 1 presents the history of scientific production on the circular economy of water. The most publications were in 2018 and 2020, with 9 and 16 publications, respectively.

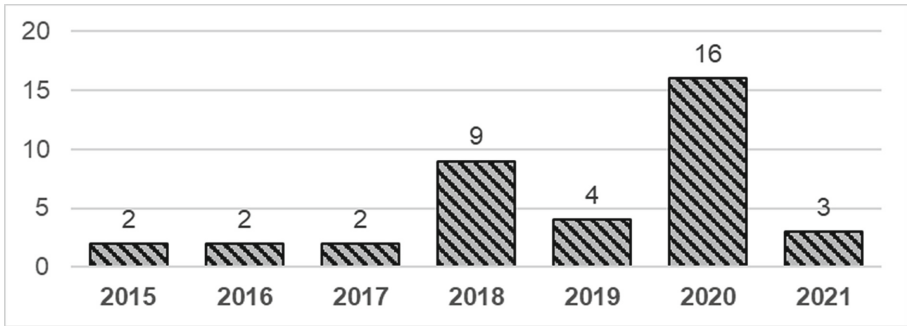


Fig. 1. History of scientific production on Circular Economy of Water.

In Table 2, the most relevant journals, considering the index that calculates the total number of citations divided by the number of articles. The Journal of Cleaner Production stands out as the leading journal that publishes on the subject under study has a JCR index of 7.246.

Table 2. The most relevant Journals on the subject.

Ranking	Journals	JCR	No. of articles	Quotes	Index
1	Journal Of Cleaner Production	7,246	6	324	54,0
2	Science Of The Total Environment	6,551	1	41	41,0
3	Water Science And Technology	1,638	1	35	35,0
4	Journal Of Environmental Management	5,647	2	53	26,5
5	Advanced Science	15,84	1	26	26,0
6	Technological And Economic Development Of Economy	2,194	1	26	26,0
7	Journal Of Material Cycles And Waste Management	1,974	1	25	25,0
8	Future Of Food-Journal On Food Agriculture And Society	–	1	13	13,0

(continued)

Table 2. (continued)

Ranking	Journals	JCR	No. of articles	Quotes	Index
9	Comparative Economic Research-Central And Eastern Europe	–	1	10	10,0
	Journal Of Hazardous Materials	9,038	1	10	10,0
	Waste Management	5,448	1	10	10,0

Table 3 presents the ten most relevant articles on the circular economy of water considering the InOrdinatio index. It is observed that the leading publications on the subject were published in the last five years. Therefore, it can be considered a current topic.

Table 3. Articles identified on Circular Economy of Water.

Ranking	Article title	Authors/Year	InOrdinatio
1	Two life cycle assessment (LCA) based methods to analyse and design complex (regional) circular economy systems. Case: making water tourism more sustainable	[16]	265,007
2	Sewer-mining: A water reuse option supporting circular economy, public service provision and entrepreneurship	[5]	123,006
3	Circular economy model for recycling waste resources under government participation: a case study in industrial wastewater circulation in china	[17]	116,016
4	Circular economy model framework in the European water and wastewater sector	[8]	115,002
5	LCA of greywater management within a water circular economy restorative thinking framework	[18]	111,007
6	Integrated circular economy and education model to address aspects of an energy-water-food nexus in a dairy facility and local contexts	[19]	105,007
7	Policy narratives of circular economy in the EU - Assessing the embeddedness of water and land in national action plans	[20]	102,007
8	Micropollutants in Lake Como water in the context of circular economy: A snapshot of water cycle contamination in a changing pollution scenario	[3]	100,009

(continued)

Table 3. (continued)

Ranking	Article title	Authors/Year	InOrdinatio
9	Environmental sustainability in the food-energy-water-health nexus: A new methodology and an application to food waste in a circular economy	[21]	100,005
10	Enhancing a Transition to a Circular Economy in the Water Sector: The EU Project WIDER UPTAKE	[6]	100,003

In Fig. 2, the Word Cloud of the titles and keywords of the ten most relevant articles are presented, highlighting the words ‘Circular’, ‘Economy’, and ‘Water’, demonstrating that these words are aligned with the theme proposed in the research. Words like ‘Assessment’, ‘Waste’, ‘Wastewater’, and ‘Analysis’ stand out.

**Fig. 2.** Word clouds of titles and keywords of the ten most relevant articles on the topic.

Entering the integrative analysis of the studies, Scheepens, Vogtländer and Brezet [16] proposed the eco cost model applied to identify the potential adverse effects on circular business models in the sustainable aquatic tourism segment. With the application of the model, it was possible to identify satisfactory results concerning the product in the environmental aspect. However, it obtained unsatisfactory results in the social aspect concerning the client.

The research by Makropoulos et al. [5] discussed the various forms of water reuse techniques to understand their strengths and weaknesses. One of the techniques tested was sewage mining, which carried out a pilot test. In this study, two tools were identified that assist in planning to estimate the amount of non-potable water energy consumed and identify sites for installing sewage mining units. Therefore, it is seen as an opportunity for small and medium-sized companies to offer this type of service. It is concluded that sewage mining is seen as a valid alternative to meet the demand for drinking water.

The study by Shen, Li and Wang [17] presents a systematic economic model to assess issues related to the circular economy. The study was carried out in China, and its aim was industrial wastewater, which identified a gap between the price charged and the

cost of water processing. The authors highlight the importance of government in matters relating to taxation and taxes.

Smol, Adam and Preisner [8] proposal is a circular economy model related to water, considering reduction, recovery, reuse, recycling, and rethinking consumption. In addition to considering the technological aspects, this proposal includes social and organisational issues. The model can evaluate and evolve aspects of the circular economy of water.

The study by Dominguez et al. [18] sought a life cycle assessment to compare three water reuse scenarios to identify the most environmentally correct technology. The research findings indicate that photovoltaic photocatalysis technology powered by sunlight has the lowest environmental impact, thus becoming an outlet for greywater reuse.

The research by Kilkış and Kilkış [19] aimed to relate educational models towards circular economic systems seeking a more sustainable future. The research aim was a dairy with biogas production in Turkey that a university created. Scenarios relating to renewable energy sources were analysed. Based on the results obtained, students became more involved in classes, visualised possible paths that do not harm natural resources and prepared professionals with sustainable concerns from university.

Fidelis et al. [20] proposal analysed how land and water are incorporated in the circular economy plan issued in 2015 and 2020 in the European Union. The results indicate that water and land do not arise as concerns compared to waste and materials. He also noted that the circular economy theory stresses the importance of water and land. However, this has not been happening according to the results presented in practice. For the circularity of water to occur, countries must have robust public policies for protection.

The study by Castiglioni et al. [3] investigated lagoons in Switzerland and Italy, which were contaminated; the results showed that public policies could influence the use of chemicals in their drugs.

The recent research by Slorach et al. [21] presented a new methodology to quantify the environmental impacts of food production in a circular economy context, which considers energy, water and health from the perspective of life cycle assessment. The main findings of the research identified that in the context studied, the issue of circularity cannot necessarily be considered environmentally sustainable. The methodology proved efficient for elaborating policies and organisations towards environmental impacts.

The study by Mannina et al. [6] sought to discuss the barriers to transforming the circular water economy. Barriers related to technological, organisational, social, economic and regulatory issues were identified. However, these barriers must be considered in public policies seeking to recover resources.

The circular economy was related to the life cycle assessment [16, 18, 21], techniques related to water reuse and recovery [3, 5, 6, 17, 18], education models [19] and Strategy [20]. The research object was sustainable tourism [16], public area [3, 5, 6, 8, 17, 20], entrepreneurship [5], manufactures [19], and food waste [21].

After the integrative analysis of the studies, it was possible to generate insights and propose a research agenda to direct future research, as follows:

- (i) Due to the high energy consumption in greywater photocatalysis, identify new renewable energy sources to use this technology [18].

- (ii) LCA effectively assesses environmental aspects, but it is necessary to include in-depth analyses of technologies and economic issues to carry out a sustainable treatment for greywater [18].
- (iii) Expand the proposal presented by Kilkış and Kilkış [19] in other contexts, as students will already be familiar with circular economy issues and, consequently, these students, being agents of change, will be able to direct them to more sustainable paths.
- (iv) It is suggested that future studies follow the guidelines of Fidélis et al. [20] and analyse other contexts, countries such as China, India and the USA that consume a significant amount of water.
- (v) The model proposed by Slorach et al. [21] is a robust multi-criteria analysis methodology that can assess environmental impacts in different contexts.
- (vi) It is suggested that the methodology proposed by Slorach et al. [21] social and economic aspects are added, thus assessing all aspects of sustainability.
- (vii) Based on the insights of Mannina et al. [6], it is suggested that a review of the scientific production be carried out that seeks to identify technologies related to processes that can recover water.

Even after the analysis is carried out, it is important to reinforce that the discussions on the subject are not exhausted. On the contrary, there is a long way to be researched, and it was possible to identify the contexts which are being investigated considering the circular economy of water, highlighting the importance of circularity. Furthermore, it was possible to point out future paths for research on the subject.

4 Final Considerations

Given the analysis carried out, the general aim of the research was achieved since it was possible to carry out an analysis of the scientific production on the circular economy of water. The Web of Science database identified 38 articles on the circular economy of water, in which the years 2018 and 2020 were the years with the most publications. The Journal Of Cleaner Production is a prominent journal that publishes articles on the subject in question.

With the calculation of the InOrdinatio index, it was possible to identify the ten most relevant articles on the circular economy of water, which, through Word Cloud, it was possible to identify the words contained in the titles and keywords aligned with the focus of the research.

The integrative analysis made it possible to survey the contexts already studied, demonstrating that the circular economy is related to assessing the life cycle, techniques related to the reuse and recovery of water, education models and strategic issues. The researched contexts were mainly related to the public area, tourism, entrepreneurship and manufacturing.

It is essential to emphasise the importance of research related to water since the concern with this resource has been observed. The discussions are far from being exhausted; therefore, a proposal for a future agenda was presented that indicates the direction for future research about the theme.

The present research has the following limitations: (i) only the Web of Science database was considered; (ii) only the strings “circular economy” AND “water” were used; and (iii) only the ten most relevant articles were analysed.

Finally, based on the limitations presented, future studies are suggested: (i) carry out a literature review that considers other databases, such as Scopus and ScienceDirect; (ii) consider other strings to make the search more comprehensive; and (iii) seek to analyse all the articles that are identified on the subject.

References

1. Ritchie, H., Roser, M.: Water use and stress. Published online at OurWorldInData.org. (2017). <https://ourworldindata.org/water-use-stress>. Accessed 10 May 2021
2. UNESCO: Water for People, Water for Life. World Water Dev Rep. 36 (2003)
3. Castiglioni, Sara, et al.: Micropollutants in lake como water in the context of circular economy: a snapshot of water cycle contamination in a changing pollution scenario. *J. Hazard. Mater.* **384**, 121441 (2020). <https://doi.org/10.1016/j.jhazmat.2019.121441>
4. World Bank TWB: Water Resources Management (2017). Accessed 10 May 2021
5. Makropoulos, C., Rozos, E., Tsoukalas, I., Plevri, A., Karakatsanis, G., Karagiannidis, L., et al.: Sewer-mining: a water reuse option supporting circular economy, public service provision and entrepreneurship. *J. Environ. Manage.* **216**, 285–298 (2018). <https://doi.org/10.1016/j.jenvman.2017.07.026>
6. Mannina, G., Badalucco, L., Barbara, L., Cosenza, A., Di Trapani, D., Gallo, G., et al.: Enhancing a transition to a circular economy in the water sector: the EU project wider uptake. *Water (Switzerland)* **13**(7), 1–18 (2021)
7. ONU O das NU. Plataforma Agenda 2030 Acelerando as transformações para a Agenda 2030 no Brasil (2015). <http://www.agenda2030.org.br/>. Accessed 10 May 2021
8. Smol, M., Adam, C., Preisner, M.: Circular economy model framework in the European water and wastewater sector. *J. Mater. Cycles Waste Manage.* **22**(3), 682–697 (2020). <https://doi.org/10.1007/s10163-019-00960-z>
9. De-la-Torre-Ugarte-Guanilo, M.C., Takahashi, R.F., Bertolozzi, M.R.: Revisão sistemática: noções gerais. *Rev da Esc Enferm da USP.* **45**(5), 1260–1266 (2011)
10. Ercole, F.F., de Melo, L.S., Alcoforado, C.L.G.C.: Integrative review versus systematic review. *Reme Rev Min Enferm.* **18**(1), 9–11 (2014)
11. Rother, E.T.: Revisão sistemática X revisão narrativa. *Acta Paul Enferm.* **20**(2), v–vi (2007)
12. Visser, M., van Eck, N.J., Waltman, L.: Large-scale comparison of bibliographic data sources: scopus, web of science, dimensions, crossref, and microsoft academic (2020). https://doi.org/10.1162/qss_a_00112
13. Pagani, R.N., Mauricio, L., De, R.M.: Avanços na composição da Methodi Ordinatio para revisão sistemática de literatura. *Ciência da Informação.* **46**(2), 161–187 (2018)
14. Pagani, R.N., Kovaleski, J.L., Resende, L.M.: Methodi Ordinatio: a proposed methodology to select and rank relevant scientific papers encompassing the impact factor, number of citation, and year of publication. *Scientometrics* **105**(3), 2109–2135 (2015). <https://doi.org/10.1007/s11192-015-1744-x>
15. Soares, C.B., Hoga, L.A., Peduzzi, M., Sangaleti, C., Yonekura, T., Silva, D.R.A.D., et al.: Revisão Integrativa versus Revisão Sistemática. *Reme Rev Min Enferm.* **8**(1), 102–106 (2010). http://www.scielo.br/pdf/rlae/v12n3/v12n3a14%0Ahttp://www.scielo.br/scielo.php?script=sci_arttext&pid=S0102-311X2007000400002&lng=pt&tlng=pt%0Ahttp://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-07072008000400018&lng=pt&tlng=pt%0Ahttp://www.ncbi

16. Scheepens, A.E., Vogtländer, J.G., Brezet, J.C.: Two life cycle assessment (LCA) based methods to analyse and design complex (regional) circular economy systems. Case: Making water tourism more sustainable. *J. Clean. Prod.* **114**, 257–268 (2016). <https://doi.org/10.1016/j.jclepro.2015.05.075>
17. Shen, K.W., Li, L., Wang, J.Q.: Circular economy model for recycling waste resources under government participation: a case study in industrial wastewater circulation in China. *Technol. Econ. Dev. Econ.* **26**(1), 21–47 (2020)
18. Dominguez, S., Laso, J., Margallo, M., Aldaco, R., Rivero, M.J., Irabien, Á., et al.: LCA of greywater management within a water circular economy restorative thinking framework. *Sci. Total Environ.* **621**, 1047–1056 (2018). <https://doi.org/10.1016/j.scitotenv.2017.10.122>
19. Kılıç, Ş., Kılıç, B.: Integrated circular economy and education model to address aspects of an energy-water-food nexus in a dairy facility and local contexts. *J. Clean. Prod.* **167**, 1084–1098 (2017). <https://doi.org/10.1016/j.jclepro.2017.03.178>
20. Fidélis, T., Cardoso, A.S., Riaz, F., Miranda, A.C., Abrantes, J., Teles, F., et al.: Policy narratives of circular economy in the EU – Assessing the embeddedness of water and land in national action plans. *J. Clean. Prod.* **288**, 125685 (2021)
21. Slorach, P.C., Jeswani, H.K., Cuéllar-Franca, R., Azapagic, A.: Environmental sustainability in the food-energy-water-health nexus: a new methodology and an application to food waste in a circular economy. *Waste Manag.* **113**, 359–368 (2020). <https://doi.org/10.1016/j.wasman.2020.06.012>



Meso and Macroporosity in Carbonaceous Materials Prepared by Thermal Treatment from Lignocellulosic Wastes

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Abstract. This work analyses the improvement of the macroporous structure of coals made from olive wood waste (OWW) by means of thermal treatment between 400 °C and 900 °C. These coals will be used in the Biomethanization or Anaerobic Digestion process of wet residual biomass, as they act as bacteriological adherents, immobilising the microorganisms that participate in this process and increasing its energy yield.

The carbonaceous adherents have been characterised by elemental analysis, mercury porosimetry, adsorption isotherms and SEM. The yield of the carbonisation process varies between 39.73% and 21.52%. For samples carbonised at 400 °C the yield is usually higher than for those carbonised between 600 °C and 900 °C.

The carbonisation temperature has a major influence on the porosity distribution in the meso- and macropore regions, and not so much the treatment time. In the mesopore region, in general, the porosity distribution is more heterogeneous, with the volume of mesoporosity increasing with increasing carbonisation temperature, according to: 900 °C > 600 °C > 400 °C.

However, as far as macropores are concerned, the size distribution is much more homogeneous and the volume of macroporosity decreases with increasing carbonisation temperature, being the sample prepared at 400 °C for 15 min showing the highest porosity development, with a total volume of 0.60 cm³ g⁻¹.

Keywords: Charcoal · Bacteriological adherent · Biomethanization

1 Introduction

The worldwide crisis, the scarcity of food reserves and the generation of polluting waste are the main challenges we face at this time to achieve socio-economic and environmental sustainability [1, 2].

The large quantities of waste generated by industrial/agricultural production processes negatively affect the natural environment [3, 4].

Anaerobic digestion (AD) is a promising technology because of its ability to degrade much of this type of organic matter and transform it into two value-added by-products, biogas (renewable energy) and a nutrient-rich digested effluent that can act as fertiliser or compost. The future of the biogas facility is a factory where value is created from previously wasted materials; this ensures sustainability of the environment and potential for financial gain for the local community. The flexibility of the anaerobic digestion system and its ability to digest a multitude of organic feedstocks, while producing a significant range of products ensures the role of anaerobic digestion and biogas in the circular economy [5].

For this technology to become more attractive and widespread, it is necessary to develop pre-treatments that increase the energy yield of the reaction and improve the profitability of a biogas plant. One of the pre-treatments to be investigated is the addition of carbonaceous materials from low-cost agricultural waste [6].

So far, most of the materials that have been used for this purpose are activated carbon, zeolite, bentonite, mineral wool, polyurethane, polyacrylate, polyethylene, and even straw as a biofilm carrier [7]. In all cases, the pore size distribution (porosity) and the pore size of the supporting medium are determining factors since these pores must be of a size suitable for colonization by the methanogenic bacteria population (whose size is about 1 μm per bacterium cell, that is, the size of macropores).

However, the common problem of all these products that increase the surface available for bacterial adhesion is that their high costs are prohibitive for application in industrial scale AD plants.

To overcome these issues, recently, biochar, which are carbonaceous materials from organic waste, are being manufactured and it has been shown that the addition of these biochars improves the AD process because they improve the removal of chemical oxygen demand (COD) and reduce the lag phase of methanogenesis, leading to higher CH_4 production [8, 9]. Furthermore, the application of biochar in AD also improves the elemental composition of the solid digestate (AD residue), which can be further processed and used as fertiliser in the agricultural field [10].

Biochar also offers advantages over other additives considering its various physicochemical characteristics, governed by feedstock types, synthesis temperature, modification/activation methods, etc. [11–13].

In addition, biochar has other applications, such as catalyst support, battery electrodes, capacitors and in biomedicine. Therefore, for these and other applications, it is becoming increasingly evident that the charcoal material used must possess not only a high degree of surface area development and microporosity, but also significant meso- and macropore contents.

In the present work, as a starting point for future research, the influence of temperature and carbonisation residence time on the development of meso- and macroporosity is

investigated using Olive Wood Waste (OWW) as a starting material, in order to add it to the Anaerobic Digestion process, as the biochar acts as bacteriological adherent, immobilising the micro-organisms involved in this process and increasing its energy yield.

2 Materials and Methods

2.1 Sample Preparation

The lignocellulosic starting material used in the preparation of the carbonised products was OWW.

After the collection or reception of this material, firstly, size reduction and sieving was carried out, selecting the particle size fraction between 1 and 2 mm. Then, using a cylindrical tube furnace (Carbolite), the materials were heated in N_2 atmosphere (gas, $\varphi = 100 \text{ mLmin}^{-1}$) at different temperatures of 400, 600 and 900 °C for different times (15 min, 30 min, 2 h, 6 h) (Fig. 1). The heating rate of the furnace from room temperature to the maximum heat treatment temperature (MHTT) was 10 °C min^{-1} .

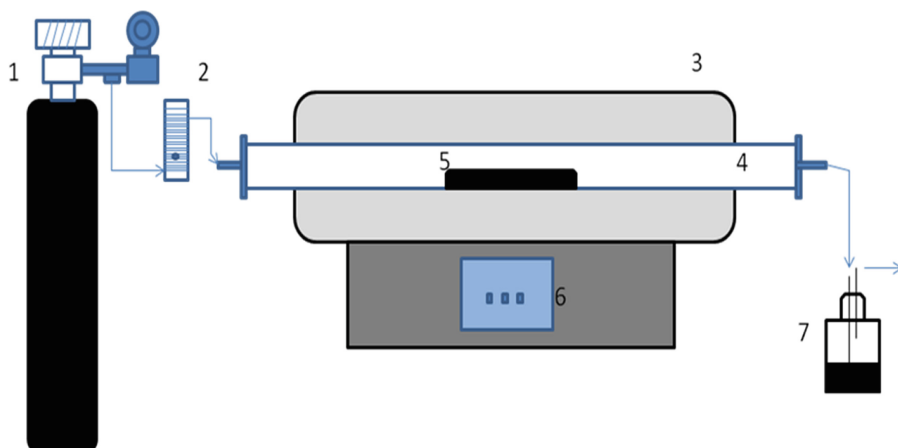


Fig. 1. Schematic of the experimental system used in the physical activation: 1) Synthetic nitrogen; 2) Rotameter; 3) Oven; 4) Reactor; 5) Sample holder; 6) Temperature programmer; 7) Gas condensation system.

Table 1 shows the notations assigned to the samples and the performance values of the sample preparation process. The samples thus prepared were characterised by elemental analysis, mercury porosimetry, adsorption isotherms and Scanning Electron Microscopy (SEM).

Table 1. Preparation of samples. Notations and yields.

Source material	MHTT */°C	Time (h)	Notation	Performance (%)
Olive wood (OWW)	400	0.25	C4-OWW-15	32.15
	400	0.5	C4-OWW-30	39.73
	400	2	C4-OWW-2	36.20
	400	6	C4-OWW-6	34.00
	600	0.25	C6-OWW-15	26.25
	600	0.5	C6-OWW-30	25.37
	600	2	C6-OWW-2	24.92
	600	6	C6-OWW-6	25.54
	900	0.25	C9-OWW-15	24.15
	900	0.5	C9-OWW-30	26.34
	900	2	C9-OWW-2	26.80
	900	6	C9-OWW-6	21.52

(*) MHTT, maximum heat treatment temperature.

2.2 Morphology and Texture

The carbonaceous adsorbents were characterized morphologically and texturally.

Electron microscope images were obtained using a model Quanta 3D FEG (FEI Company) scanning electron microscope operating in high-vacuum mode under an accelerating voltage ranging from 0.1 to 30 kV, and an Everhart Thornley detector for secondary electrons. Several SEM images of randomly chosen particle regions and grains were acquired for each sample at different magnifications.

In addition, N₂ adsorption at 196 °C was determined, together with mercury porosimetry, and mercury and helium density measurements. In particular, the N₂ adsorption isotherm was determined on 0.118 g of sample in a Quantachrome Autosorb⁻¹ device after degassing the aliquot at 120 °C for 12 h. For the porosimetry, a Quantachrome PoreMaster 60 porosimeter was used, with ~ 0.326 g of charcoal sample put into the glass holder which was then evacuated by means of an oil pump before filling with mercury, determining the sample's mercury density from knowing the previously calibrated glass holder volume and the density of liquid mercury at the working temperature (Fig. 2). The helium density was measured in a Quantachrome stereopycnometer, using ~ 3 g of sample.

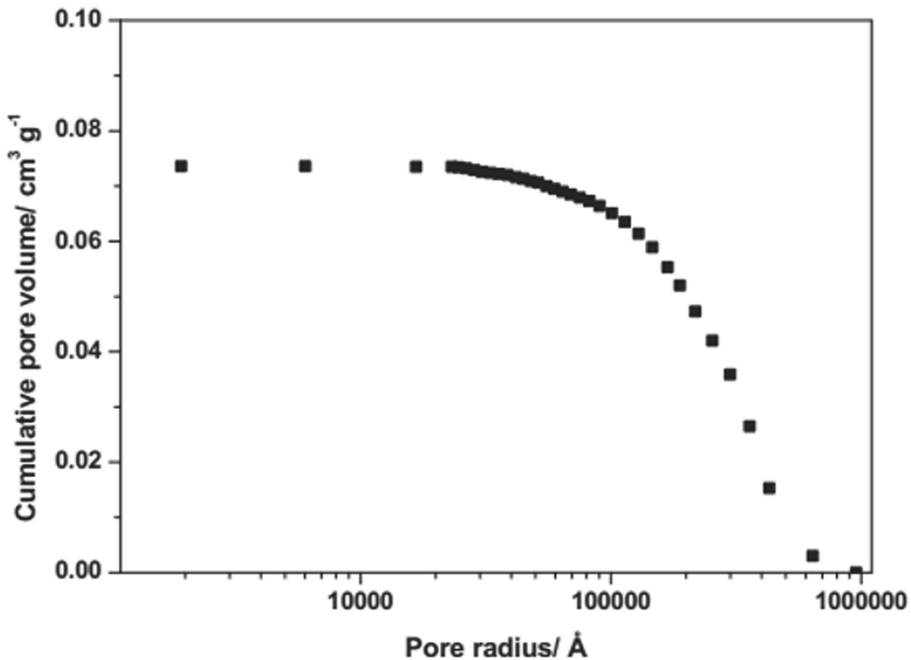


Fig. 2. Curve of mercury intrusion against pore radius.

3 Results and Discussion

3.1 Sample Preparation

The yield values of the sample preparation process are given in Table 1. In the case of heat-treated samples, the yield depends mainly on the MHTT. Thus, the yield values for samples carbonised at 400 °C are between 32.15% and 39.73%, while the yield is $\approx 27.5\%$ for most of the samples heated at 600 °C and 900 °C.

As can be seen, the yield decreases very significantly with increasing MHTT between 400 and 900 °C. However, the decrease in yield is much larger between 400 °C and 600 °C than between 600 °C and 900 °C.

These results are in perfect agreement with the mechanism usually postulated for the pyrolysis of lignocellulosic materials, according to which when these materials are heated in an inert atmosphere, depolymerisation and devolatilisation occurs.

This process results in a large mass loss below 400–450 °C, which is accompanied by a progressive aromatisation in the residual solid.

From the point of view of the change in mass, it is generally considered that at a temperature of 600 °C the pyrolysis process is largely completed. At higher temperatures, the aromatic character in the char is further increased, as hydrogen is released and rings are melted, and the mass loss is smaller and quite similar at the different heat treatment temperatures.

The yield values obtained for the different starting materials (Table 1) are not very different from those generally obtained in previous studies, also carried out with lignocellulosic materials [14–16].

3.2 Elemental Analysis

The elemental analysis data determined for the carbonised products at 400 °C, 600 °C and 900 °C are presented in Table 2. As expected, the most abundant chemical constituent in all samples is carbon, whose content ranges from 82.49% of C6-OWW-2 to 59.01% of C9-OWW-2. The hydrogen and nitrogen contents are much lower, ranging around 2.8% and 0.8% (average values) respectively.

The sulphur content is practically zero in all carbonisates. Finally, the oxygen content is also high in relative terms.

Table 2. Elemental analysis data of selected samples.

Samples	%C ± SD	% H ± SD	%N ± SD	% S ± SD	%O*
C4-OWW-15	70.58 ± 1.11	4.39 ± 0.44	0.30 ± 0.01	0.05 ± 0.00	24.68
C4-OWW-30	63.95 ± 2.37	5.24 ± 0.00	0.14 ± 0.08	0.05 ± 0.00	30.62
C4-OWW-2	65.93 ± 1.23	2.85 ± 1.04	0.19 ± 0.11	0.04 ± 0.00	30.99
C4-OWW-6	66.39 ± 0.35	3.48 ± 0.04	0.49 ± 0.01	0.04 ± 0.00	29.60
C6-OWW-15	79.94 ± 0.63	3.23 ± 0.16	0.35 ± 0.02	0.03 ± 0.00	16.45
C6-OWW-30	79.84 ± 1.26	2.96 ± 0.06	0.52 ± 0.13	0.05 ± 0.00	16.63
C6-OWW-2	82.49 ± 0.33	3.10 ± 0.71	0.55 ± 0.17	0.05 ± 0.00	13.81
C6-OWW-6	81.22 ± 0.12	2.43 ± 0.02	0.46 ± 0.02	0.05 ± 0.00	15.84
C9-OWW-15	77.91 ± 1.66	1.96 ± 0.05	0.84 ± 0.13	0.04 ± 0.00	19.25
C9-OWW-30	73.53 ± 0.88	1.84 ± 0.02	1.02 ± 0.04	0.04 ± 0.00	23.57
C9-OWW-2	59.01 ± 2.11	1.80 ± 0.13	1.97 ± 0.11	0.04 ± 0.00	37.18
C9-OWW-6	64.76 ± 1.00	0.72 ± 0.11	2.97 ± 0.03	0.05 ± 0.00	31.50

* Obtained by difference.

3.3 Meso and Macroporous Textures

The cumulative pore volume versus pore radius curves obtained for the twelve sample series under study can be seen in Fig. 3 and the values of the meso and macropore volumes (V_{me-p} , V_{ma-p}) together with the density values measured by mercury displacement (ρ_{Hg}) have been compiled in Table 3.

Simply by looking at Fig. 3, it is evident that the carbonisation temperature has a very important influence on the porosity distribution in the meso- and macropore regions. In the mesopore region, in general, the porosity distribution is wider for samples prepared

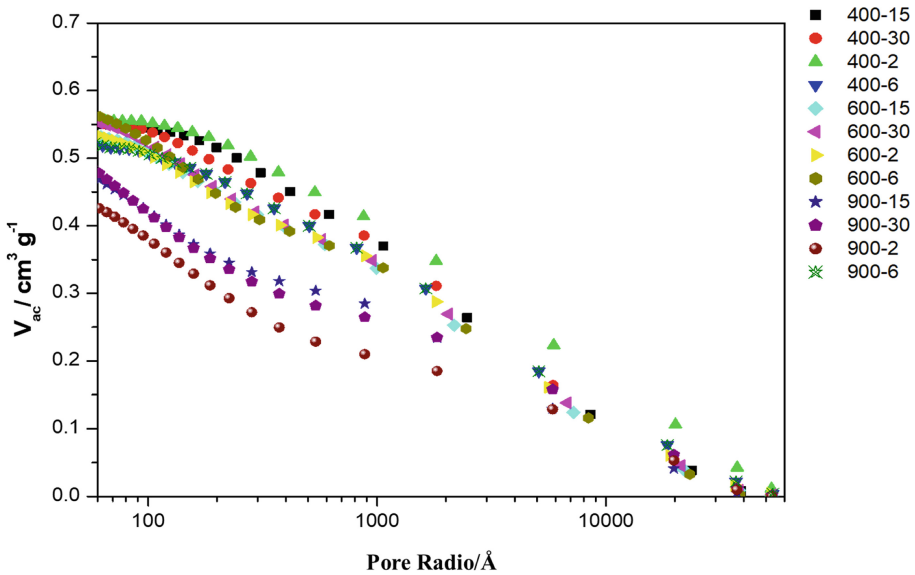


Fig. 3. Mercury intrusion curves.

at higher temperatures than at lower temperatures, i.e. at 900 and 600, and narrower when samples are prepared at lower temperatures, i.e. at 400 °C.

As for the macropores, the pore size distribution is much more homogeneous and the volume of macroporosity decreases with increasing carbonisation temperature (Table 3).

Therefore, it is evident that, in general, the maximum porosity development is achieved when the MHTT is lower. The sample with the highest pore content is sample C4-OWW-15, with a total volume of $0.60 \text{ cm}^3 \text{ g}^{-1}$, and it is also much more macro than mesoporous ($V_{\text{ma-p}} = 0.50 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{me-p}} = 0.10 \text{ cm}^3 \text{ g}^{-1}$).

Table 3. Meso- and macropore volumes. Mercury densities.

Samples	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	$V_{\text{me-p}}$ (cm^3/g)	$V_{\text{ma-p}}$ (cm^3/g)	ρ_{Hg} (g/cm^3)
C4-OWW-15	54.2	0.00	0.03	0.10	0.50	0.70
C4-OWW-30	369.0	0.03	0.03	0.09	0.48	0.87
C4-OWW-2	6.9	0.00	0.02	0.08	0.50	1.15
C4-OWW-6	61.2	0.01	0.06	0.10	0.45	1.01
C6-OWW-15	0.0	0.00	0.05	0.11	0.44	0.72
C6-OWW-30	0.0	0.00	0.06	0.14	0.44	0.76
C6-OWW-2	12.10	0.00	0.03	0.13	0.43	0.69
C6-OWW-6	8.7	0.00	0.13	0.18	0.43	0.75

(continued)

Table 3. (continued)

Samples	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	$V_{\text{me-p}}$ (cm^3/g)	$V_{\text{ma-p}}$ (cm^3/g)	ρ_{Hg} (g/cm^3)
C9-OWW-15	90.7	0.03	0.10	0.19	0.35	0.76
C9-OWW-30	54.6	0.01	0.06	0.23	0.32	0.91
C9-OWW-2	59.6	0.02	0.06	0.20	0.27	1.07
C9-OWW-6	6.8	0.00	0.04	0.23	0.26	1.06

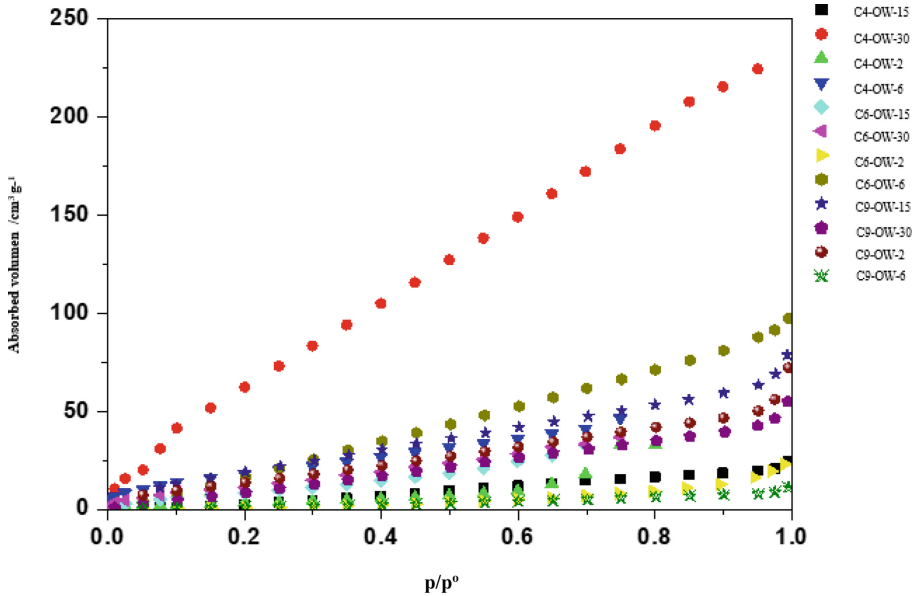
**Fig. 4.** N_2 adsorption isotherms at $-196\text{ }^\circ\text{C}$

Table 3 also includes the values of the bulk density (ρ_{Hg}) of the samples. As can be observed, and according to the physical meaning of this density [16], a lower ρ_{Hg} is compatible with the presence in the sample of lighter fractions and a more developed total porosity. Therefore, we observe in Table 3, how a lower ρ_{Hg} corresponds to a larger pore volume. However, it is observed that in sample C6-OWW-2 this is not the case and this may be due to the heating at such a high temperature ($600\text{ }^\circ\text{C}$), which can also cause shrinkage and even closure of the narrow porosity generated due to the pyrolysis process (Fig. 4).

4 Conclusions

The results obtained in the present study on the preparation of meso and/or macroporous carbonaceous materials from olive wood by thermal methods have led to the following conclusions:

The performance of the preparation process of carbonised products depends much more on the maximum temperature than on the heat treatment time.

The sulphur content is generally zero in the samples.

The distribution of mesopores is widest in samples prepared at high temperatures 900 °C and 600 °C and narrowest when samples are prepared at 400 °C.

The carbonisation temperature influences the development of macroporosity, being higher the lower the MHTT, with sample C4-OWW-15 being much more macro than mesoporous, with $V_{\text{ma-p}}$ equal to $0.50 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{me-p}}$ at $0.10 \text{ cm}^3 \text{ g}^{-1}$.

Finally, the properties and functionalities of charcoal depend significantly on the pyrolysis process and, according to the literature, charcoal has a huge potential to be used in AD as an additive to increase its productivity.

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References

1. Elsayed, M., et al.: Innovative integrated approach of biofuel production from agricultural wastes by anaerobic digestion and black soldier fly larvae. *J. Clean. Prod.* **263**, 121495 (2020). <https://doi.org/10.1016/j.jclepro.2020.121495>
2. Kumar, M., Sun, Y., Rathour, R., Pandey, A., Thakur, I.S., Tsang, D.C.W.: Algae as potential feedstock for the production of biofuels and value-added products: opportunities and challenges. *Sci. Total Environ.* **716**, 137116 (2020). <https://doi.org/10.1016/j.scitotenv.2020.137116>
3. Kumar, M., et al.: Lignin valorization by bacterial genus *Pseudomonas*: state-of-the-art review and prospects. *Bioresour. Technol.* 124412 (2020). <https://doi.org/10.1016/j.biortech.2020.124412>
4. Thakur, I.S., Kumar, M., Varjani, S.J., Wu, Y., Gnansounou, E., Ravindran, S.: Sequestration and utilization of carbon dioxide by chemical and biological methods for biofuels and biomaterials by chemoautotrophs: opportunities and challenges. *Bioresour. Technol.* **256**, 478–490 (2018). <https://doi.org/10.1016/j.biortech.2018.02.039>
5. Fagerström, A., Al Seadi, T., Rasi, S., Briseid, T.: The role of Anaerobic Digestion and Biogas in the Circular Economy. *IAE Boienergy. Task 37* (2018)
6. Sánchez-Sánchez, C., González-González, A., Cuadros-Salcedo, F., Cuadros-Blázquez, F.: Using low-cost porous materials to increase biogas production: a case study in Extremadura (Spain). *J. Clean. Prod.* **198**, 1165–1172 (2018). <https://doi.org/10.1016/j.jclepro.2018.07.079>
7. Ward, A.J., Hobbs, P.J., Holliman, P.J., Jones, D.L.: Optimisation of the anaerobic digestion of agricultural resources. *Biores. Technol.* **99**, 7928–7940 (2008)
8. Wang, C., Liu, Y., Gao, X., Chen, H., Xu, X., Zhu, L.: Role of biochar in the granulation of anaerobic sludge and improvement of electron transfer characteristics. *Bioresour. Technol.* **268**, 28–35 (2018). <https://doi.org/10.1016/j.biortech.2018.07.116>
9. Sánchez-Sánchez, C., González-González, A., Cuadros-Salcedo, F., Gómez-Serrano, V., Cuadros-Blázquez, F.: Charcoal as a bacteriological adherent for biomethanation of organic wastes. *Energy* **179**, 336–342 (2019). <https://doi.org/10.1016/j.energy.2019.04.192>

10. Shen, Y., Forrester, S., Koval, J., Urgan-Demirtas, M.: Yearlong semi-continuous operation of thermophilic two-stage anaerobic digesters amended with biochar for enhanced biomethane production. *J. Clean. Prod.* **167**, 863–874 (2017). <https://doi.org/10.1016/j.jclepro.2017.05.135>
11. Luz, F.C., Cordiner, S., Manni, A., Mulone, V., Rocco, V.: Biochar characteristics and early applications in anaerobic digestion-a review. *J. Environ. Chem. Eng.* **6**, 2892–2909 (2018). <https://doi.org/10.1016/j.jece.2018.04.015>
12. Luz, F.C., et al.: *Ampelodesmos mauritanicus* pyrolysis biochar in anaerobic digestion process: evaluation of the biogas yield. *Energy* **161**, 663–669 (2018). <https://doi.org/10.1016/j.energy.2018.07.196>
13. Masebinu, S.O., Akinlabi, E.T., Muzenda, E., Aboyade, A.O.: A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. *Renew. Sustain. Energy Rev.* **103**, 291–307 (2019). <https://doi.org/10.1016/j.rser.2018.12.048>
14. Gómez-Serrano, V., Pastor-Villegas, P., Pérez-Florindo, A., Duran-Valle, C., Valenzuela-Calahorra, C.: FT-IR study of rockrose and of char and activated carbon. *J. Anal. Appl. Pyrol.* **36**, 71–80 (1996)
15. Gómez-Serrano, V., Pfriz-Almeida, F., Durán-Valle, C.J., Pastor-Villegas, J.: Formation of oxygen structures by air activation. A study by FT-IR spectroscopy. *Carbon* **37**, 1517–1528 (1999)
16. Durán-Valle, C.J., Gómez-Corzo, M., Pastor-Villegas, J., Gómez-Serrano, V.: Study of cherry stones as raw material in preparation of carbonaceous adsorbents. *J. Anal. Appl. Pyrolysis* **73**, 59–67 (2005)



Green Biomaterials: Applications of Plant-Derived Biofilms

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Abstract. The use of plants as biomaterials holds an extremely high potential. The application of plant materials in several areas of agri-food, biotechnology, engineering, and health sciences is of enormous interest to the green and low-carbon industry. Plants are a source of polysaccharides, essential oils, and vitamins, among other components that can be used in the formulation of composite materials of plant origin. Polysaccharides with good mechanical properties include alginate, cellulose, and pectin, which already have been applied for drug delivery, production of artificial extracellular matrices, and 3D scaffolds for tissue engineering. Moreover, the extracts and essential oils of some plant's present anti-inflammatory, antioxidant, and antibacterial capacity. These bioactive properties can be transferred to applications in the most diverse areas, through encapsulation of plant extracts/essential oils into biofilms or polymeric matrices. Plant-derived biomaterials are generally highly available and easy to produce at low costs. Although biodegradable, they decompose at slower rates than other biomaterials due to their enzymatic resistance. In addition, biomaterials of plant origin show high biocompatibility, low immunogenicity, and additional nutritional value. Here, we briefly review on the applications of enriching and encapsulating plant derived extracts into natural polysaccharide-based materials. The use of natural materials is an efficient solution towards higher environmental sustainability and a greener economy.

Keywords: Biomaterials · Plants-derived materials · Polysaccharide-based biofilms · Alginate · Pectin · Cellulose · Encapsulation

1 Introduction

Natural polymers such as polysaccharides are valuable assets due to their biodegradability, biocompatibility, and nontoxicity. Polysaccharides of algae and plant origin such as alginate, cellulose and pectin are outstanding materials that can be accessible at low prices and show tunable physicochemical and mechanical properties, along with high renewability and recyclability. Moreover, functional additives such as antimicrobial compounds, antioxidants, minerals, vitamins, and other bioactive molecules can be added into polysaccharide-based matrices to synergistically extend the favorable properties of these biopolymers. Thus, the functionality of polysaccharide-based materials can be further enhanced through incorporation of other green materials, such as plant extracts, polyphenols, and essential oils, to be used in a wide range of applications (e.g.: smart materials, biosensing, wastewater treatment, bioremediation, food coating, wound dressing, drug delivery and tissue engineering) (Fig. 1).

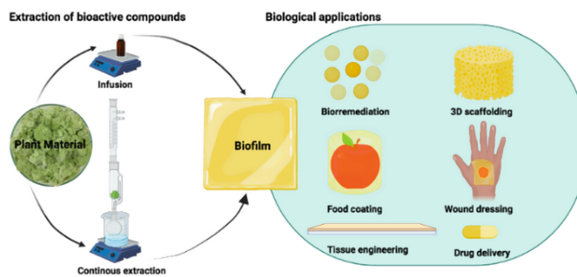


Fig. 1. Polysaccharide-based enriched biofilms: extraction of compounds, preparation of biofilms and fields of application (e.g., bioremediation, drug delivery, wound dressing, tissue engineering, food coating and 3D scaffolding). Image produced by E. Foulquié with Biorender.com.

1.1 Alginate-Based Enriched Biofilms

Alginates are unbranched polysaccharides extracted from brown marine algae and bacteria [1]. Alginates are copolymers of β -D-mannuronic acid (M) and α -L-guluronic acid (G) linked in an irregular block-wise manner, that differs significantly according to the source of extraction [1]. Alginates can undergo gelation and form transparent water-soluble structures that can be processed into hydrogels, microspheres, foams, fibres, gauze, or sponges [2]. Crude extracts, essential oils, and bioactive molecules of plant origin can be loaded into these alginate-based supports, towards the production of highly versatile eco-friendly structures, with various applications [3–13]. In what regards food coating, alginate-based edible coatings enriched with *Ficus hirta* fruit extract inhibited the growth of pathogenic fungi in Nanfeng mandarins, stored for 100 days at 6 °C [3]; while alginate coatings enriched in pomegranate peel extract delayed the ripening of guavas (*Allahabad safeda*) during 20 days of storage, at 10 °C [4]. Additionally, other authors have shown that alginate coatings enriched with green tea and grape-seed presented antiviral properties against norovirus and hepatitis A virus [5], whereas

alginate-based formulations enriched with lemongrass essential oil showed antimicrobial activity against several fungi [6] and were able to preserve the firmness and colour of 'Rocha' pears [7]. Moreover, extracts of olive leaves loaded into alginate microbeads formed edible matrices with improved thermal stability, as detected by differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) [8]. Also, mangoes packed into multilayer coatings composed of cinnamon essential oils and alginate, were able to preserve the firmness, edible content, and commercial value of the fruits, after 14 days, at 25 °C [9]; while edible coatings containing oregano essential oil improved the shelf life of tomatoes, by reducing endogenous microbial growth over 14 days, at room temperature [10].

In what concerns tissue engineering, calcium enriched alginate hydrogels were able to promote neovascularization and osteochondral repair [11]. In addition, Pereira et al. showed that *Aloe vera* enriched alginate films presented suitable properties for wound healing and drug delivery applications [1, 12]. In what respects bioremediation for instance, an alginate-coated magnetic nanocluster with high adsorption capacity and high selectivity for inorganic mercury has been developed as a nanosorbent tool for wastewater treatment [13]. Thus, given their versatility and sustainability, the use of alginate-based enriched biomaterials continues to grow and find new applications among several fields.

1.2 Pectin-Based Enriched Biofilms

Pectins are plant cell wall polysaccharides mainly composed by galacturonic acid [14]. Depending on composition, structure, and molecular weight, pectins can be classified in homogalacturonans, rhamnogalacturonans, xylogalacturonans, arabinogalactans and arabinans [14]. Pectins can undergo gelation and work as emulsifying, gelling, stabilizing and thickening agents, with several uses amongst various fields, given their low cost, non-toxicity, high stability, and biocompatibility [14–22].

Edible pectin films hold good mechanical and barrier properties to apply in the coating or packaging of fruits and vegetables [14, 15]. Pectin films enriched with black-currant pomace powder, for instance, were used to minimize food production losses and to increase the functional properties of food coatings and wrappers [16]. In addition, edible pectin coatings enriched with clove essential oil (CEO) were also able to act as seafood preservatives [17]. These CEO pectin-based films inhibited bacterial growth; improved the water holding capacity; prevented lipid oxidation and extended the shelf life and textural attributes of bream fillets, by at least 15 days, under refrigeration [17]. Moreover, pectin-based biomaterials also hold great potential for biomedical applications, given their natural prebiotic, dietetic, hypoglycemic, hypocholesterolemic, and anti-cancer effects [18–20]. In what regards bioremediation, pectin-based materials have been applied with success to pollutants removal due to their special ability to coordinate divalent cations [21, 22]. Commercial citrus pectin, sugar beet pulp pectin and sweet potato pectin have been able to remove heavy metals (Pb(II), Cu(II), Co(II) and Zn(II)) and organic dyes from aqueous solution [21, 22].

1.3 Cellulose-Based Enriched Biofilms

Cellulose is a natural polymer of D-glucose connected by $\beta(1 \rightarrow 4)$ glycosidic bonds [23, 24]. Cellulose is present in all plants to provide for structure and mechanical integrity. Cellulose fibers are highly hydrophilic, have low density, are nonabrasive and can be used as natural thickeners, binders, emulsifiers, suspending agents, surfactants, lubricants, stabilizers, and additives [23, 24]. Guava fruits coated with cellulose films, for instance, showed increased firmness, color maintenance, and reduced ripeness, for 13 days, at room temperature [25]. Additionally, cellulose-based films impregnated with esters of caffeic acid were able to show increased antioxidant activity and antimicrobial effects against various microorganisms [26]; while cellulose-based composites containing natural antimicrobials were able to inhibit the growth of food spoilage and pathogenic microorganisms such as *Listeria monocytogenes*, as well as to enhance the safety and quality of cold smoked salmon [27] and of individually packaged hot dogs [28]. Moreover, cellulose nanoparticles showed enhanced antioxidant activities of curcumin and ascorbyl dipalmitate when employed in packaging films [29]; and showed antimicrobial activity when applied to mature-green tomatoes (inhibition of *Salmonella Montevideo* and maintenance of color and firmness) stored at 20 °C, for 18 days [30]. Furthermore, cellulose-based-nanomaterials have also been used for tissue engineering, wound dressing, and 3D bioprinting [23, 24, 31], as well as for bioremediation and water treatment, by membrane filtration, catalytic degradation, absorption, adsorption, and/or disinfection [32–34]. Cellulose-based hydrogels formed by sonochemistry, for instance, use green-chemistry processes (with reduced reaction steps and chemical reagents), that also promote biocompatibility [35].

2 Conclusions

A sustainable and recycle-based society can be developed through the use of renewable and bio-based materials. Multifunctional alginate-based, pectin-based, and cellulose-based enriched structures can be applied to several industrial fields. These natural materials are key to promote environmental sustainability and continue to amaze by their properties and advantages, either presented separately or as conjugated biocomposites.

References








1. Pereira, R., Carvalho, A., Vaz, D., Gil, M., Mendes, A., Bártolo, P.: Development of novel alginate-based hydrogel films for wound healing applications. *Int. J. Biol. Macromol.* **52**, 221–230 (2013)
2. Deng, Y., Shavandi, A., Okoro, O., Nie, L.: Alginate modification via click chemistry for biomedical applications. *Carbohydr. Polym.* **270**, 118360 (2021)
3. Chen, C., Nie, Z., Wan, C., Chen, J.: Preservation of Xinyu Tangerines with an edible coating using *Ficus hirta* Vahl Fruits Extract-Incorporated Chitosan. *Biomolecules* **9**, 46 (2019)
4. Nair, M., Saxena, A., Kaur, C.: Effect of chitosan and alginate-based coatings enriched with pomegranate peel extract to extend the postharvest quality of guava (*Psidium guajava* L.). *Food Chem.* **240**, 245–252 (2017)

5. Fabra, M., Falco, I., Randazzo, W., Sanchez, G., Lopez-Rubio, A.: Antiviral and antioxidant properties of active alginate edible films containing phenolic extracts. *Food Hydrocoll.* **81**, 96–103 (2018)
6. Cofelice, M., Cinelli, G., Lopez, F., Di Renzo, T., Coppola, R., Reale, A.: Alginate-Assisted Lemongrass (*Cymbopogon nardus*) Essential Oil Dispersions for Antifungal Activity. *Foods* **10**, 1528 (2021)
7. Gago, C., et al.: The Effect of nanocoatings enriched with essential oils on “Rocha” pear long storage. *Foods* **9**, 240 (2020)
8. Flamminii, F., et al.: Alginate-based microparticles structured with different biopolymers and enriched with a phenolic-rich olive leaves extract: a physico-chemical characterization. *Curr. Res. Food Sci.* **4**, 698–706 (2021)
9. Yin, C., Huang, C., Wang, J., Liu, Y., Lu, P., Huang, L.: Effect of Chitosan- and alginate-based coatings enriched with cinnamon essential oil microcapsules to improve the postharvest quality of mangoes. *Materials (Basel)* **12**, 2039 (2019)
10. Pirozzi, A., Del Grosso, V., Ferrari, G., Donsi, F.: Edible coatings containing oregano essential oil nanoemulsion for improving postharvest quality and shelf life of tomatoes. *Foods* **9**, 1605 (2020)
11. Xing, J., et al.: Gellan gum/alginate-based Ca-enriched acellular bilayer hydrogel with robust interface bonding for effective osteochondral repair. *Carbohydr. Polym.* **270**, 118382 (2021)
12. Pereira, R., Tojeira, A., Vaz, D., Mendes, A., Bártolo, P.: Preparation and characterization of films based on alginate and *Aloe Vera*. *Int. J. Polym. Anal. Charact.* **16**, 449–464 (2011)
13. Deepuppha, N., Thongsaw, A., Rutnakornpituk, B., Chaiyasith, W., Rutnakornpituk, M.: Alginate-based magnetic nanosorbent immobilized with aptamer for selective and high adsorption of Hg²⁺ in water samples. *Environ. Sci. Pollut. Res. Int.* **27**, 12030–12038 (2020)
14. Lara-Espinoza, C., Carvajal-Millán, E., Baladrán-Quintana, R., López-Franco, Y., Rascón-Chu, A.: Pectin and pectin-based composite materials: beyond food texture. *Molecules* **23**, 942 (2018)
15. Brito, T., Carrajola, J., Gonçalves, E., Martelli-Tosi, M., Ferreira, M.: Fruit and vegetable residues flours with different granulometry range as raw material for pectin-enriched biodegradable film preparation. *Food Res. Int.* **121**, 412–421 (2019)
16. Kurek, M., et al.: Characterization of food packaging films with blackcurrant fruit waste as a source of antioxidant and color sensing intelligent material. *Molecules* **26**, 2569 (2021)
17. Nisar, T., Yang, X., Alim, A., Iqbal, M., Wang, Z., Guo, Y.: Physicochemical responses and microbiological changes of bream (*Megalobrama ambycephala*) to pectin-based coatings enriched with clove essential oil during refrigeration. *Int. J. Biol. Macromol.* **124**, 1156–1166 (2019)
18. Li, D., et al.: Pectin in biomedical and drug delivery applications: a review. *Int. J. Biol. Macromol.* **185**, 49–65 (2021)
19. An, H., et al.: Pectin-based injectable and biodegradable self-healing hydrogels for enhanced synergistic anticancer therapy. *Acta Biomater.* **131**, 149–161 (2021)
20. Maxwell, E., Belshaw, N., Waldron, K., Morris, V.: Pectin—an emerging new bioactive food polysaccharide. *Trends Food Sci. Technol.* **24**, 64–73 (2012)
21. Thakur, S., Chaudhary, J., Kumar, V., Thakur, V.: Progress in pectin-based hydrogels for water purification: trends and challenges. *J. Environ. Manage.* **238**, 210–223 (2019)
22. Li, J., et al.: The role of surface functional groups of pectin and pectin-based materials on the adsorption of heavy metal ions and dyes. *Carbohydr. Polym.* **276**, 118789 (2021)
23. Wang, C., et al.: The application status of nanoscale cellulose-based hydrogels in tissue engineering and regenerative biomedicine. *Front. Bioeng. Biotechnol.* **9**, 732513 (2021)
24. Karki, S., Gohain, M., Yadav, D., Ingole, P.: Nanocomposite and bio-nanocomposite polymeric materials/membranes development in energy and medical sector: A review. *Int. J. Biol. Macromol.* **193**, 2121–2139 (2021)

25. Francisco, C., et al.: Shelf-life of guavas coated with biodegradable starch and cellulose-based films. *Int. J. Biol. Macromol.* **152**, 272–279 (2020)
26. Saelo, S., Assatarakul, K., Sane, A., Suppakul, P.: Fabrication of novel bioactive cellulose-based films derived from caffeic acid phenethyl ester-loaded nanoparticles via a rapid expansion process: RESOLV. *J. Agric. Food Chem.* **64**, 6694–6707 (2016)
27. Neetoo, H., Mahomoodally, F.: Use of antimicrobial films and edible coatings incorporating chemical and biological preservatives to control growth of *Listeria monocytogenes* on cold smoked salmon. *Biomed. Res. Int.* **2014**, 534915 (2014)
28. Franklin, N., Cooksey, K., Getty, K.: Inhibition of *Listeria monocytogenes* on the surface of individually packaged hot dogs with a packaging film coating containing nisin. *J. Food Prot.* **67**, 480–485 (2004)
29. Sonkaew, P., Sane, A., Suppakul, P.: Antioxidant activities of curcumin and ascorbyl dipalmitate nanoparticles and their activities after incorporation into cellulose-based packaging films. *J. Agric. Food Chem.* **60**, 5388–5399 (2012)
30. Zhuang, R., Beuchat, L., Chinnan, M., Shewfelt, R., Huang, Y.: Inactivation of *Salmonella montevideo* on tomatoes by applying cellulose-based edible films. *J. Food Prot.* **59**, 808–812 (1996)
31. Tarrahi, R., Khataee, A., Karimi, A., Yoon, Y.: The latest achievements in plant cellulose-based biomaterials for tissue engineering focusing on skin repair. *Chemosphere* **288**, 132529 (2022)
32. Rana, A., Mishra, Y., Gupta, V., Thakur, V.: Sustainable materials in the removal of pesticides from contaminated water: Perspective on macro to nanoscale cellulose. *Sci. Total Environ.* **797**, 149129 (2021)
33. Zhao, X., Wahid, F., Cui, J., Wang, Y., Zhong, C.: Cellulose-based special wetting materials for oil/water separation: a review. *Int. J. Biol. Macromol.* **185**, 890–906 (2021)
34. Jiang, Z., Ho, S., Wang, X., Li, Y., Wang, C.: Application of biodegradable cellulose-based biomass materials in wastewater treatment. *Environ. Pollut.* **290**, 118087 (2021)
35. Liu, Y., Li, S., Wang, Z., Wang, L.: Ultrasound in cellulose-based hydrogel for biomedical use: from extraction to preparation. *Colloids surf B, Biointerfaces* **212**, 112368 (2022)



Gasification Potential of Solid Recovered Fuels (SRF) Produced in Portugal

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Abstract. According to the European standard EN ISO 21640:2021, Solid Recovered Fuels (SRF) is defined as solid fuel made from non-hazardous waste used for energy recovery, that can be produced by specific waste, municipal solid waste, industrial waste, commercial waste, construction and demolition waste and sewage sludge. These fuels can be used to generate electricity and/or thermal energy, promoting a low-carbon and circular economy. In recent years, the use of SFR has expanded to other interesting and promising fields, such as gasification or combined gasification and pyrolysis.

This work aims to clarify the terminology of SRF, identify the production of different fractions of SRF in Portugal (industrial or municipal-waste source), classify each fraction, according to its potential and identify the main barriers to the gasification of SRF. For that, it was performed several physical-chemical analyses on SRF samples from different origins and locations.

Results showed that in Portugal, SRF production can be divided into two typologies considering their origin: SRF from urban wastes or SRF from industrial wastes. Regarding the urban wastes SRF, in 2019 it was produced 683 tons in Portugal. The main physical-chemical characteristics demonstrate levels of moisture between 33.9% and 39.14%, low heating values (LHV) in order of 12 MJ/kg, and high content of heavy metals, sulfur, and chlorine. Regarding the SRF from industrial wastes, it was identified an annual production of above 200 thousand tons in 2019. The characteristics or physical-chemical composition of this type of SRF, namely low percentage of humidity (15–17.3%), LHV in order of 19.43 MJ/kg, and also the low concentration of heavy metals, confirm the potential use of this product in gasification processes.

Keywords: Solid Recovered Fuels (SRF) · Gasification · Waste-to-Energy

1 Introduction

Wastes represent nowadays, one of the major concerns for modern societies and for the environment, either by the wastage of raw materials and also by the existence of poor

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management systems that contaminate the groundwater and air, and therefore, change the environment irreversibly [1, 2]. Waste gasification, particularly Solid Recovery Fuels (SRF) gasification, despite its challenges, presents itself as a viable option for its recovery [2]–[4]. However, there are still many barriers to the extensive development and use of SRFs, namely, their classification and terminology and the legislation on its uses. Portuguese legislation (NP 4486:2008) [5] uses the terminology Refused Derived Fuel (RDF), which can be misinterpreted only to the production of a fuel from treated municipal solid wastes (MSW) fraction in Mechanical and Biological Pre-Treatment (MBT) plants. RDF refers to poorer quality materials, with high moisture content (between 15 and 30%) and lower calorific value. The SRF is presented as a more homogeneous set of materials, of better quality and high calorific value, which meets classification and specification requirements defined by a national or international standard.

According to the European standard EN ISO 21640:2021, Solid Recovered Fuels (SRF) is defined as solid fuel made from non-hazardous waste used for energy recovery, that can be produced by specific waste, municipal solid waste, industrial waste, commercial waste, construction and demolition waste and sewage sludge. These fuels can be used to generate electricity and/or thermal energy, promoting a low-carbon and circular economy. In recent years, the use of SRF has expanded to other interesting and promising fields, such as gasification or combined gasification and pyrolysis. Among them, gasification could play an important role in greenhouse gas (GHG) emissions-cutting due to its pollution minimization effects, higher overall efficiency and ability to produce syngas with multiple exploration methods [6].

Conventional gasification is a thermal process, which converts carbonaceous materials, such as MSW, into syngas using a gasifying agent or agents, such as steam, carbon dioxide or air. These gasifying agents react with chars, tars, and gases to produce syngas. The main syngas products (carbon monoxide (CO) and hydrogen (H₂)) are used to produce heat and electricity or are converted into liquid hydrocarbons. Syngas composition also presents methane (CH₄) and carbon dioxide (CO₂) that are produced and play an important role in gasification reactions [3, 4, 7].

Gasification occurs through a sequence of complex thermochemical reactions that include: Drying zone, Pyrolysis or thermal decomposition zone, Partial oxidation or combustion zone and Reduction zone (utilization of gasifying agents).

Gasification is one of the thermochemical conversion processes through which it is possible to convert solid or liquid fuels into gases or other useful chemicals. This process takes place at high temperatures in the presence of a gassing agent which may simply be air, oxygen, water vapor, or a mixture thereof may also be used [3, 4].

Waste gasification can be highlighted as the best-proven technique to increase the energy efficiency of waste-to-energy processes and optimize their contribution to national and global climate and energy goals. Therefore, the utilization of SRF as a robust endogenous resource can respond to a range of problems associated with waste management, making it possible to: minimize the deposition of wastes in landfill; contribute to national self-sufficiency in energy production; contribute to the reduction of greenhouse gases through the reduction of CH₄ emission from landfill; diversify the sources of fuels [8].

The main objectives of this work, are to clarify the terminology of SRF, identify the production of different fractions of SRF in Portugal (industrial or municipal-waste source), classify each fraction, according to its potential and identify the main barriers to the gasification of SRF. For that, it was performed several physical-chemical analyses on SRF samples from different origins and locations.

2 Terminology and Classification of SRF

Despite the numerous advantages of using SRF, there are some barriers to dissemination in global terms, of which, it can be highlighted the continuing confusion in terminology.

Solid fuels recovered from non-hazardous waste are identified in different countries by different terms (e.g., CSS, CDR, CDR-Q, RPF, SBS, CSR,), shipped with different waste codes, and an ambiguous use of the terms RDF and SRF still occurs. SRF is largely produced and traded as waste, different countries labelling it with different waste codes based on local waste legislation. An end-of-waste of SRF is allowed in some countries (e.g., Austria, Italy) if the fuels produced comply with specific and mandatory requirements legally set. The latest ISO 21640 [9], development based on the European standard, confirms that definition of SRF, emphasizes the origin of waste that are not more suitable for efficient reuse and recycling of materials and provides shared rules (classification and specification requirements) that can be applied in different countries to identify a secondary fuel as SRF. Therefore, ISO 21640 is nowadays assumed as a reference to distinguish between RDF and SRF. The process of classification according to the ISO 21640 is presented in Fig. 1.

SRF and RDF are locally produced in MT and MBT plants from individual or mixed streams of municipal (MSW), commercial (CW), industrial (IW) and construction and demolition (CDW) wastes that can differ in their share of residual fractions and, based on this, also in their elemental composition [10]–[12].

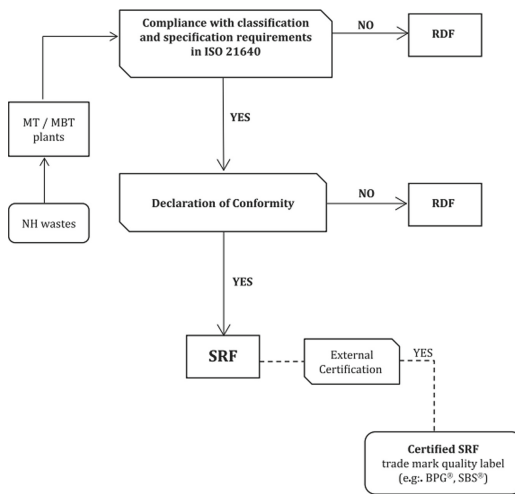


Fig. 1. Proposed approach to distinguish between RDF and SRF according to ISO 21640:2021.

Different types and degrees of treatment are applied by the producers to the input waste streams that modify to some extent their properties and determine the achievable yield in waste derived fuels, in both quantitative and qualitative terms. Based on this, SRF is a classified secondary fuel in compliance with the conformity, classification and specification requirements of ISO 21640, and RDF is a secondary fuel that don't meet the requirements of ISO 21640.

3 SRF Production

In Portugal, SRF production can be divided into two typologies considering their origin: SRF from urban wastes or SRF from industrial wastes. The first one, is a relatively crude material, produced by shredding pre-sorted municipal solid waste (MSW). Before the MSW can enter the SRF production process, valuable commodities such as paper, metal, glass and wood should have been removed for recycling. On the other hand, SRF from industrial wastes, is a much more refined resource, produced to a defined quality specification.

3.1 SRF Produced from Urban Wastes

Regarding to Municipal Solid Wastes (MSW) management, Portugal is still facing some problems. MSW management is currently dominated by landfilling, but Portugal has invested in many other treatment options including incineration, composting and more recently in Mechanical and Biologic Treatment (MBT) technology. This choice made by Portugal regarding MSW treatment processes, namely mechanical and biological treatments, is based on the recognition that they have great potential in terms of reducing the deposition of MSWs in landfills, a significant increase in recycling rates and significant reduction in greenhouse gas emissions, fundamental aspects for the pursuit of national and community goals. Thus, the treatment of MSWs results in a set of waste that can be recycled material, organic or incinerated with energy production [13].

According to the strategic plan for urban wastes (PERSU 2020), the main material streams in the urban waste management systems (SGRU) in Portugal and Portuguese autonomous regions, are presented as shown in Fig. 2. In the specific case of SRFs, according to the same document, there is an increase in the diversion of refuse and rejects from landfills, around 300 thousand tons per year, through the production of fuels derived from waste [14].

According to the data available in the most recent Annual Report on Urban Waste [13], there has been a decrease in the production of material for SRF over the last few years. The production of SRF material in sorting facilities, mechanical treatment and mechanical and biological treatment units declared by the SGRU between the years 2015 and 2019 is shown in Table 1.

These data show a slight increase in the SRF produced in 2019 compared to 2018. However, the low production of SRF, when compared to the years 2015 and 2016, can be explained by the unavailability of waste management operators in the reception of this material from the SGRU, a consequence of the high levels of humidity that they normally present. The national SRF market suffered an evident stagnation in terms of

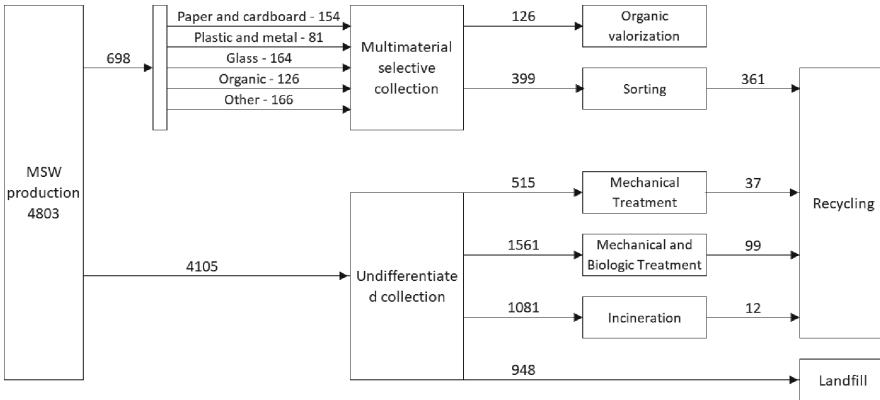


Fig. 2. Main waste streams (thousands of tons) in urban waste management systems in Portugal (including autonomous regions) in 2020. Adapted from [14].

processing and dispatch due to the difficulty of selling SRFs. The SGRUs consider that the preparation and drying operation is not feasible due to factors such as high investments needed to prepare the SRFs; high transport costs due to the high dispersion of cement plants; and also because the Portuguese cement industry uses a much higher amount of imported SRF than those produced by the SGRUs, arguing that material from the other EU Member States has the required technical and economic conditions [15].

Table 1. SRF production from urban wastes (tons) [13].

SRF from urban wastes	Total				
	2015	2016	2017	2018	2019
Sorting facilities	1308	0	0	15	7
Mechanical treatment	33750	21042	0	0	0
Mechanical and biological treatment	72564	467	379	385	677
SRF production units	6943	0	0	0	0
Total	114566	21509	379	400	683

3.2 SRF Production from Industrial Wastes

Regarding to SRF produced from industrial wastes, a lack of official indicators was observed. The information relating to the Strategic Plan for Industrial Waste (PESGRI), or the National Plan for the Prevention of Industrial Waste (PNAPRI) were not available for consultation. However, the scope of the most recent information referred to in these documents does not exceed the year 2015, which would constitute a somewhat outdated scenario. To obtain some relevant information regarding SRF from industrial waste,

a search by code LER 191210 was carried out on the SILOGR platform (Licensing Information System for Waste Management Operations). As a result of this search, 48 licensed operators were identified, from which only 7 were identified as effective products or with installed capacity for SRF production (Table 2).

Table 2. Industrial waste management entities producing SRF.

Operator	Annual Production (ton/year)	Obs.
Company 1	40000	-
Company 2	9257*	*Quantity produced in 2019
Company 3	-	Production capacity 70000 ton/year
Company 4	-	Production capacity 80000 ton/year
Company 5	150269*	*Quantity produced in 2019

Based on this, an annual production of above 200 thousand tons in 2019 was identified. It was also identified that some companies decided to stop the SRF production in 2019, and some of them, dismantled their production unit.

4 Physical-Chemical Characterizations of SRF

The designation Refused Derived Fuel (RDF) encompasses different alternative fuels since it is possible to produce fuels based on different residues without obeying specific characteristics. In order to minimize the generalization of the term and to regularize the production of SRF, the European Commission published in 2006 the specification CEN/TS 15357. The European Committee for Standardization (CEN) is the entity that promotes the development of European standards that aim to establish important criteria for products, services, and processes, ensuring that they are suitable for the purposes for which they are intended. According to this organization a Solid Recovered Fuel (SRF) is defined as solid fuel prepared from non-hazardous waste to be utilized for energy recovery in incineration or co-incineration plants and meeting the classification and specification requirements defined in CEN/TS 15359 standard and identified in the European waste list by the code 191210. This standard is transposed to national legislation by the NP 4486:2008 normative [5], which intends to frame the SRF in the national panorama through the definition of classification criteria and methodology of physical and chemical characterization involved in quality management. According to this standard, only fuels prepared from non-hazardous waste and meeting the admissibility standards can be classified as solid recovered fuel (SRF). The respective classification system is based on the threshold value of three properties: Low heating value (LHV) – economical parameter; chlorine content – technical parameter; mercury content – environmental parameter. The calorific value that the material has represents the amount of heat released by combustion per unit weight of the waste. The Higher Calorific Value (HHV) translates the calorific value when the water vapor formed returns to its initial state, that is, it condenses,

returning the heat of vaporization [16]. The Lower Calorific Power (LHV) is the one in which the heat of vaporization is not returned, that is, it escapes with the combustion gases through the chimney [16], which is what happens in industrial installations. This latter characterizes and enables the suitability of materials/waste for energy recovery. According to Table 3, the classification is defined by assigning a value, on a scale of 1 to 5, to each parameter.

Table 3. SRF classification system (NP 4486/2008) [5].

Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Chlorine content (Cl)	Mean	% (dry base)	≤ 0.2	≤ 0.6	≤ 1.0	≤ 1.5	≤ 3
Low Heating Value (LHV)	Mean	MJ/kg (as received)	≥ 25	≥ 20	≥ 15	≥ 10	≥ 3
Mercury content (Hg)	Median (80 th percentile)	mg/MJ (as received)	≤ 0.02	≤ 0.03	≤ 0.08	≤ 0.15	≤ 0.5
			≤ 0.04	≤ 0.06	≤ 0.16	≤ 0.30	≤ 1.00

The values regarding the lower heating value and chlorine content are obtained using the arithmetic mean, corresponding to the mercury content, the maximum value of the range comprised by the median and the 80th percentile. The same standard also imposes mandatory and optional specifications. Mandatory specifications include class code, origin, particle shape, ash content, moisture content, calorific value, and chemical properties. Voluntary specification properties are biomass content, physical composition, fuel preparation, and physical properties such as mass density, volatile content, and chemical properties for major and minor elements.

4.1 SRF from Urban Wastes

To obtain a comparative view of the characteristics of the SRF produced in several regions of Portugal, data relating to various producing entities are presented. These data were collected from the available bibliography and are related to the years between 2010 to 2020. Concerning the SRF produced from MSW, and according to the data available in [17] the author presents a brief characterization of SRF produced by an operator that processes non-hazardous industrial wastes and urban wastes from Lisbon metropolitan area. In this case, only SRF produced from MSW was considered. Concerning this operator, the data in the Table 4 refer to the average of the values obtained from the analysis of 42 samples collected between the months of January and June 2015.

The parameters that were assessed define the feasibility of the SRF for use in co-processing by the cement industry. As it can be observed, the moisture content presents an average value that is fixed at 39.14%, well above what is accepted by this type of industry. Also, the LHV was calculated, and the average value of 12.02 MJ/kg was recorded, which is explained by the high moisture content, taking into account the presence of a high

Table 4. Characterization of SRF produced from MSW collected from different regions of Portugal.

Parameters	Units	Lisbon metropolitan area [17]	South region [18]	Center region [18]
*Moisture content	%	39.14	33.19	35,33
Ash	%	14.68	20.20	12,42
Volatile matter	%	-	71.45	-
LHV	MJ/kg	21.23	18.46	-
*LHV	MJ/kg	12.02	-	12.83
HHV	MJ/kg	-	19.23	-
Carbon	%	-	46,79	48,77
Hidrogen	%	-	5,30	3,03
Nitrogen	%	-	1,54	1,13
Sulfur	%	-	0,19	0,30
Chlorine	%	0.83	0,53	0.53
Sodium	mg/kg	-	5200	-
Potassium	mg/kg	-	4200	-
Aluminum	mg/kg	-	6300	-
Phosphor	mg/kg	-	1600	-
Copper	mg/kg	-	100	65,00
Zinc	mg/kg	-	100	293,83
Lead	mg/kg	-	0	33,67
Vanadium	mg/kg	-	-	6,58
Chromium	mg/kg	-	-	20,92
Nickel	mg/kg	-	-	15,83
Arsenic	mg/kg	-	-	5,50
Cadmium	mg/kg	-	-	3,00
Antimony	mg/kg	-	-	17,08
Mercury	mg/kg	-	-	0,31
Manganese	mg/kg	-	-	44,33
Granulometry (>25 mm)	%	23.55	-	-
Parameters on a dry basis, except *				

amount of biodegradable residues that make up the samples. Regarding the chlorine content, it was measured on a dry basis, a value of 0.83% was recorded. The mercury content recorded was practically nil, so, according to the NP 4486/2008 standard, this SRF is classified as PCI 4; CL 3; Hg 2. Another characterization reported by [18], is related to the same kind of waste coming from south region of Portugal. The purpose was to assess the potential and feasibility of SRF for use as an alternative combustible. 10 samples from different points of the facility's internal circuit were collected. The analyzes were carried out on each of the samples, and for the purposes of presentation in this work, the average value of each parameter was calculated. According to the results presented in Table 4 and the evaluation of the author, can be assigned to this SRF the classification PCI 3; CI 2; Hg 1. Once again it can be observed high moisture contents. Regarding the LHV on a dry basis (d.b.) is even lower than the previous example. This gives a poor quality of this SRF for use as an alternative combustible. The same author [18] also presents a characterization of SRF produced from MSW collected from the center region of Portugal. The samples considered for the characterization of the SRF potential were collected in a total of 12, in the period between August 2008 and December 2009. For the purposes of presentation in this report, the average value of each parameter was calculated. The values recorded are presented in Table 4. As can be observed the moisture content is in the same order of magnitude as the samples from other locations, so keeping high values. In this case, the LHV is not measured on a dry basis, but when compared these values, it suggests that the correspondent value on a dry basis is in the same order of magnitude as other samples. According to the NP 4486:2008 and the conclusions of the author, this SRF can be classified as follows: PCI 3; CI 2; Hg 2 (for the 2008 samples); PCI 4; CI 2; Hg 2 (for the 2009 samples); PCI 4; CI 2; Hg 2 (considering all samples).

4.2 SRF From Industrial Wastes

Concerning the SRF derived from industrial wastes a physicochemical characterization of SRF produced from industrial wastes collected from the north region of Portugal and Lisbon metropolitan area was recorded. In the first case, these analyses were made according to the NP 4486:2008 standard. The results recorded are resumed in Table 5.

As it can be seen, the moisture content recorded in this case is very low, in opposite to the values obtained from SRF made from MSW. Also, the LHV is higher consider the typical values from SRF made from MSW. Despite the low metal concentration, it has high concentrations of sulfur and chlorine that could present operational problems in the thermal conversion, especially in a large-scale exploration. In order to contain these problems, a step of cleaning the gas formed through the introduction of water columns was included in the execution of the tests. The standards of extreme quality of these SRFs are reached due to the process of sorting and separation to which the non-hazardous waste of industrial origin is submitted.

These factors clearly indicate that these SRFs are excellent raw materials for the gasification process. These data can be compared with a study reported by [17] regarding to industrial wastes collected from Lisbon metropolitan area. The samples were collected between January to September 2015.

Table 5 presents the average of the values obtained from 64 samples provided by non-hazardous industrial wastes. In this case, the moisture content is higher than the previous samples, standing at 17.30%. Even so, this parameter is below 20%, which is acceptable for the industry, namely the cement industry, to use as a substitute for fossil fuels. High moisture contents may compromise the efficiency of the combustion process since it will cause a drastic reduction in the temperature inside the oven. Related to the LHV, and chlorine content, 19.4 MJ/kg, and 0.92% were recorded respectively. According to NP 4486/2008 standard this SRF is classified as PCI 3; CI 3; Hg 2.

Table 5. Characterization of SRF produced from industrial wastes collected from north region and Lisbon metropolitan area.

Parameters		Units	North region	Lisbon metropolitan area [17]
Ash		%	15.00	17.6
*Moisture content		%	5.70	17.29
LHV		MJ/kg	24.33	23.25
*LHV		MJ/kg	-	19.43
Particle size:	>25 mm	%	-	14.56
	25–50 μm	%	5.4	-
	12.5–25 μm	%	23.3	-
	6.3–12.5 μm	%	44.3	-
	3.15–6.3 μm	%	13.1	-
	<3.15 μm	%	13.9	-
Chlorine		%	0.91	0.92
Antimony		mg/kg	54.00	-
Arsenic		mg/kg	< 0.8	-
Cadmium		mg/kg	0.30	-
Lead		mg/kg	42.00	-
Cobalt		mg/kg	2.00	-
Copper		mg/kg	2970.00	-
Chromium		mg/kg	520.00	-
Manganese		mg/kg	52.00	-
Mercury		mg/kg	<0.50	-
Nickel		mg/kg	15.00	-
Tálio		mg/kg	< 0.20	-
Vanadium		mg/kg	5.00	-
Aluminum		mg/kg	-	-

(continued)

Table 5. (continued)

Parameters		Units	North region	Lisbon metropolitan area [17]
Metallic aluminum		%	0.25	-
Carbon		%	56.20	-
Hydrogen		%	7.14	-
Nitrogen		%	0.91	-
Sulfur		mg/kg	2150.00	-
Bromine		mg/kg	513.00	-
Fluorine		mg/kg	95.00	-
Specific weight		g/cm ³	0.10	-
Biomass content		%	39.70	-
Volatile matter		%	77.20	-
Parameters on a dry basis, except *				

5 Conclusions

As it was possible to verify with the execution of this work, it is possible to conclude that there is a high potential for the energy recovery of waste by gasification technologies. Regarding SRF, they can be divided into two typologies considering their origin: SRF from urban waste and SRF from industrial waste. Regarding SRFs originating from urban waste and, consequently, produced in mechanical and biological treatment units (TMB), it was found that over the last few years, there has been a large reduction in their production at national level. The low production of SRF can be explained by the unavailability of waste management operators (OGR) in receiving this material from the SGRU, as a consequence of the high humidity levels that they normally present, high investments needed to prepare the SRFs, high transport costs, and higher amount of imported SRF by cement industry. For this reason, during 2019, many existing SRF production units did not operate, and those that did not use their full processing capacity. Therefore, it appears that in 2019, 683 tons of SRF of urban origin were produced. On the other hand, there are 1.2 million tons of scrap or remaining fraction of the TMB units. The physical-chemical composition of these wastes conditions their energy recovery, mainly due to the high percentage of humidity (above 40%). Regarding the production of SRF from industrial waste, it was possible to verify the annual production of more than 200 thousand tons of SRF. The characteristics or physical-chemical composition of this type of SRF, namely, low percentage of humidity, low concentration of heavy metals and HHV, attest to the potential use of this product in gasification processes.

References

1. Waste: a problem or a resource? — European Environment Agency. <https://www.eea.europa.eu/publications/signals-2014/articles/waste-a-problem-or-a-resource>. Accessed 23 May 2022
2. Tchobanoglous, G., Kreith, F.: Handbook of Solid Waste Management, Second Edn. (2018)
3. Speight, J.G.: Handbook of Gasification Technology (2020)
4. Basu, P.: Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory (2013)
5. da Qualidade, I.P.: NP 4486:2008 - Combustíveis derivados de resíduos. Enquadramento para a produção, classificação e gestão da qualidade. Instituto Português da Qualidade, pp. 1—44 (2008)
6. Ionescu, G., Rada, E.C., Ragazzi, M., Mărculescu, C., Badea, A., Apostol, T.: Integrated municipal solid waste scenario model using advanced pretreatment and waste to energy processes. *Energy Convers. Manag.* **76**, 1083–1092 (2013). <https://doi.org/10.1016/J.ENC ONMAN.2013.08.049>
7. Speight, J.G.: Gasification of Unconventional Feedstocks. Elsevier (2014)
8. Heidenreich, S., Foscolo, P.U.: New concepts in biomass gasification. *Prog. Energy Combust. Sci.* **46**, 72–95 (2015). <https://doi.org/10.1016/J.PECS.2014.06.002>
9. ISO - ISO 21640:2021 - Solid recovered fuels — Specifications and classes. <https://www.iso.org/standard/71309.html>. Accessed 16 Mar. 2022
10. Nasrullah, M., Vainikka, P., Hannula, J., Hurme, M., Kärki, J.: Mass, energy and material balances of SRF production process. Part 3: solid recovered fuel produced from municipal solid waste. *Waste Manag. Res.* **33**(2), 146–156 (2015). <https://doi.org/10.1177/0734242X14563375>
11. Nasrullah, M., Vainikka, P., Hannula, J., Hurme, M., Kärki, J.: Mass, energy and material balances of SRF production process. Part 2: SRF produced from construction and demolition waste. *Waste Manag.* **34**(11), 2163–2170 (2014). <https://doi.org/10.1016/J.WASMAN.2014.06.009>
12. Nasrullah, M., Vainikka, P., Hannula, J., Hurme, M., Kärki, J.: Mass, energy and material balances of SRF production process. Part 1: SRF produced from commercial and industrial waste. *Waste Manag.* **34**(8), 1398–1407 (2014). <https://doi.org/10.1016/J.WASMAN.2014.03.011>
13. Marçal, A., Ferreira, C.: Relatório Anual Resíduos Urbanos 2019 (2020)
14. Ministério do Ambiente: “Plano Estratégico para os Resíduos Sólidos Urbanos 2020”, *Diário da República*, no. Persu **2020**, 1–86 (2014)
15. Vaz, A.S., et al.: PERSU2020+, Reflexão estratégica e ajustamentos às medidas do PERSU 2020. Amadora (2019)
16. Cengel, Y., Turner, R., Cimbala, J.: Fundamental of thermal fluid sciences, p. 1079 (2008)
17. de O. Caracol, P.M.: Avaliação da viabilidade dos combustíveis derivados de resíduos Caso de estudo da indústria cimenteira. Instituto Superior Técnico - Lisboa (2016)
18. dos, I., de Carvalho, R.G.: CDR, um Resíduo ou um Produto, e a sua Viabilidade Técnico-Económica: Análise do Estudo Caso. Universidade Nova de Lisboa (2011)



A Preliminary Study of the Effect of White Crowberry Extract in Yogurt Manufacturing

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Abstract. Nowadays, the consumer demands new food products, with high-protein, low-fat and rich in health-promoting compounds. Based on these requests, the Portuguese white crowberry or “camarinha” has been gaining interest due to their quality attributes like acid flavor, pleasant white color and high potential in antioxidant compounds as also observed in other wild berries, for instance, blueberries and arbutus.

The present study aims to evaluate the yogurt manufacturing by addition of the white crowberry fruits in the freeze-dried form (LIO) and the extract obtained after infusion and lyophilization (CAM), compared to a control sample without the white crowberry fruits (CTR). In all the studied yogurt sample, the determination of pH-value, solids soluble content (SSC), color (CIE L*a*b* color parameters) and total phenolic content (TPC) and sensorial analysis (global appreciation, appearance, and taste), were performed.

During the yogurt manufacturing, it was possible to observe an identical behavior on the pH-value decrease, being the fermentation process similar in both enriched yogurt samples. Also, a slight pink color was achieved in the LIO sample as compared to CTR. This slight color change was denoted by the sensorial panel that appreciated the overall product. Regarding the TP content, both the yogurts enriched with the white crowberry fruits revealed better results than the found in the CTR sample.

Overall, these results are useful to reveal the value of one endemic fruit, the Portuguese white crowberry, until today unexploited in the enrichment of one dairy product, as yogurt, a food product that reach various age groups of Society.

Keywords: “camarinha” · Bioactive · Quality · Sensorial analysis · *Corema album* L. (D.) Don

1 Introduction

The Portuguese white crowberry (*Corema album* L. (D.) Don), also known as “camarinha” is an evergreen shrub endemic of the Atlantic coast of the Iberian Peninsula. There

are two species in the genus *Corema*, the species *Corema conradii* which is native to the north American east coast, and the *Corema album* L (D.) Don, native to the western coast of the Iberian Peninsula [1]. Moreover, there is as well as subspecies in the Azores archipelago promptly named *Corema album* subsp. *Azoricum*, present in 66% of the islands and under 200 m of altitude [2]. The differences between the two species seems to be the type and leaf density as well as fruit density [3].

In overall, the Portuguese crowberry fruits are characterized by its white color, acidic flavor, and the hard seed. As observed in other wild fruits, such as blueberry and arbutus, the white crowberry fruits show a high antioxidant potential [4, 5] and their inclusion in the Diet can contribute to a diversified food and promising effect on Society health. Despite the fruits are not marketed in the large distribution chains of the Agri-food sector [6], the consumption of these is growing in the Region where they can be found, essentially in the fresh way but also in drinks, jams, and jelly products.

The aim of this study was to evaluate the impact of freeze-drying and the infusion of the Portuguese white crowberry fruits on yogurt manufacturing. For that, the yogurt fermentation process was monitored until the end and in the final product, quality attributes such as pH, soluble solids content, color, total phenolic content, and sensorial analysis were determined. The use of this unexploited natural, wild, and endemic fruits, by development of a new food product, yogurt, will be promoting the food diet of many consumers that are looking for natural foods with health benefits.

2 Materials and Methods

2.1 Collection and Infusion of the White Crowberry Fruits

The Portuguese white crowberry fruits without any visual damage nor showing signs of translucence were collected in 2020, on the 14th September, from Cabo Carvoeiro (Peniche, Portugal, see Fig. 1) and transported in a food plastic bag in a cold environment to the Research laboratory, CETEMARES. Afterwards, the white crowberry fruits were washed to remove any leaves and debris, dried using the paper towels and freeze-dried (see Fig. 2).

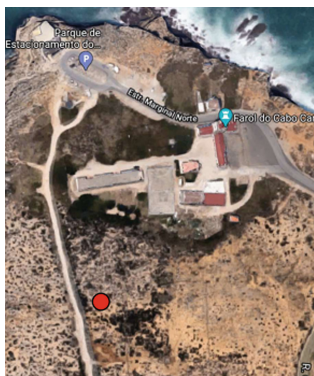


Fig. 1. Collection of the Portuguese white crowberry fruits (Peniche, Portugal, 39°21'35.2"N 9°24'20.9"W).

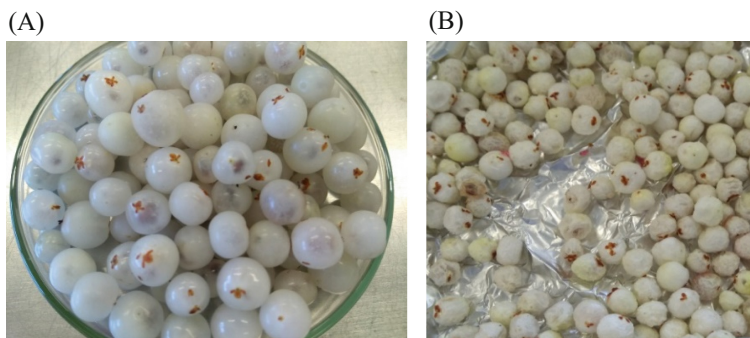


Fig. 2. Fresh (A) and freeze-dried (B) Portuguese white crowberry fruits.

2.2 Yogurt Manufacturing

The manufacturing of the enriched yogurt was performed by addition of the (a) white crowberry fruits freeze-dried crushed in small pieces and (b) after the infusion by mix with water at 95 °C in a proportion ratio of 1:20 (m:v) and leaving for 5 min. Then, the infusion was filtered, and the liquid phase was collected, freeze dried and used in enrichment of yogurt.

For the manufacturing process of yogurt, the next ingredients were used: 500 mL of pasteurized milk (“Pingo Doce”), 60 g of natural yogurt (“Pingo Doce”), 25 g of dried milk powder (“Nido”), 40 g of white granulated sugar (“Pingo Doce”) and for the yogurt enriched with the freeze-dried fruits, about 10 g were added and for the infused lyophilized near to 5 g. After the mixture, the heat treatment at 50 °C for 4 min in the cooking robot (Bimby – Vorwerk, Thermomixer 31–1) was performed. After, the mixture was transferred into sterilized jars (around 90 g per jar) and left in a pre-heated incubator at 45 °C. pH measurements were taken every half hour until a pH value of 4.5 was reached. The yogurt samples were then removed from the incubator, cooled at room temperature, and stored at 4 °C. Also, yogurt without the white crowberry fruits was produced and used as a control sample.

2.3 Methodology

2.3.1 pH and Soluble Solids Content Determination

The pH value of yogurt samples was determined using a pH meter (SP70P, SympHony, Radnor, PA, USA), after calibration according to the manufactured recommended procedure.

The soluble solids content (SSC) of the yogurt samples was measured in a refractometer (BST, RFM340 +, Kent, UK) and were expressed as °Brix.

2.3.2 Color Determination

The color of yogurt samples was evaluated according to [7] by the tristimulus colorimeter (Minolta chroma Meter, CR-400, Osaka, Japan), and after calibration with a white

standard tile ($L^* = 97.10$, $a^* = 0.19$, $b^* = 1.95$), using the illuminate D65 and observer 2°. The color parameters obtained, where the L^* values which represent the luminosity (black-white) of the samples, and a^* and b^* values, which indicate the variation of greenness to redness and blueness to yellowness, respectively.

2.3.3 Total Phenolic Content Determination

The total phenolic content (TPC) of the yogurt samples was performed using the Folin-Ciocalteu methodology [8]. Firstly, the yogurt sample was mixed with water (1:1; m:v) and kept overnight at refrigerated temperature. After, a separation was made by centrifugation at 7800 rpm during 15 min at 25 °C. Then the supernatant of sample / standard was mixed with 100 μL of Folin-Ciocalteu diluted with ultrapure water at a proportion of 1:10 (v:v). After 4 min of reaction, 80 μL of a Na_2CO_3 (7.5%, w/v) solution was added and left in the dark for 120 min at room temperature. The analysis of results was realized in a microplate (Bioteck, SynergyH1, Thermo-Scientific, Winooski, USA) and read at 750 nm. Results were expressed using the average of 9 determinations, in mg of gallic acid equivalents per gram of yogurt (mg GAE.g^{-1}), using a standard curve of gallic acid with concentrations between 0.25 to 0.050 mg.mL^{-1} .

2.3.4 Sensorial Analysis

The sensorial analysis of the manufactured yogurt's samples (CTR, LIO, and CAM) and the commercial yogurts (COM), was performed by a panel of 15 semi-trained panelists (members of the SensoMarES panel from the MARE-Polytechnic of Leiria) through the hedonic test. This consisted in identifying the sensorial quality attributes related to appearance (appearance, color), flavor (global flavor, berry flavor), taste (sweetness, texture) and global appreciation rating the numeric scale of 9-point, in yogurt samples (from low to high intensity).

2.4 Statistical Analysis

All analysis were performed in triplicate and the data was presented as average \pm standard deviation. The analysis of variance (ANOVA) of data was carried out using the StatisticaTMv.8.0 Software from Statsoft. The obtained results were considered statistically significant at a level of significance of 5% ($p\text{-value} < 0.05$), following the Tukey HSD (Honestly Significant Difference) test.

3 Results and Discussion

3.1 Manufacturing Process of Yogurt Enriched with an Extract of the White Crowberry Fruits

During the yogurt manufacturing it is expected the reduction of the pH value, representing the success of the fermentation process. At the beginning of incubation at a temperature of 45 °C, the yogurt sample with both fruits' extracts, freeze-dried and infusion lyophilized, denotes a reduced pH value compared to the CTR sample, 5.8, 5.45 and 6.4, respectively

(Fig. 3). Indeed, a reduction of the initial pH-value was achieved with both addition of fruits extracts, which remained lower in the first 90 min. After, the CTR sample reach faster the pH value expected (≈ 4.5). This pH-value was achieved after 240 min for yogurt without the crowberry extract and 300 min for both enriched yogurts.

Based on previous studies related to yogurt manufacturing, the selection of ingredients normally used is essential and preferable for the yogurt production, since some specific pH range can influence the action of some gelling agents, as reported by Grasso et al. [9] and Lück et al. [10]. Moreover, at the end of yogurt fermentation, the CAM sample denotes a sensitive texture unlike the observed in yogurt enriched with freeze-dried fruits and was confirmed by the sensorial analysis performed.

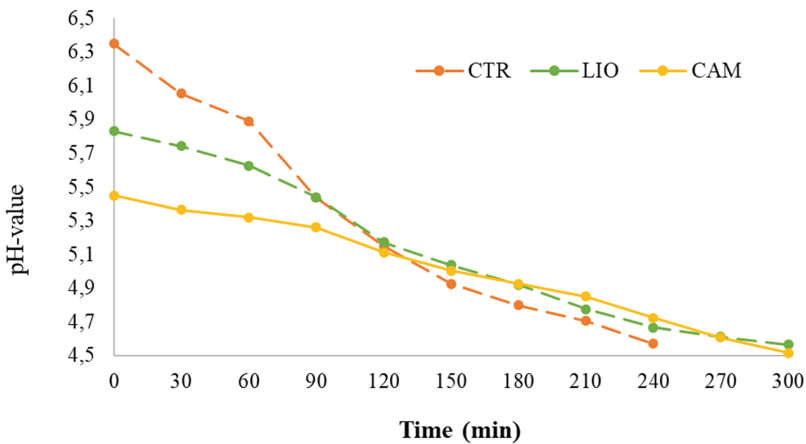


Fig. 3. Evolution of pH value during fermentation of the yogurt samples (CTR, LIO, CAM).

3.2 Instrumental Analysis and Sensorial Evaluation of Yogurt Quality

The manufacturing of yogurt without (CTR) and with the white crowberry fruits' extract (LIO and CAM) resulted in similar products with a slight difference regarding the physical properties such as pH, soluble solids content (SSC), color and total phenolic content (TPC) of the sample, as can be observed in Table 1.

Despite the identical pH-value of both yogurt samples, the SSC differ significantly ($p < 0.05$, Tukey test) between them. This difference could be associated with the extended period of time of yogurt fermentation, where the consumption of sugars was higher compared to the CTR sample. Also, the natural and fresh white crowberry fruits showed a low sugar composition as reported by Jacinto et al. [1], and Andrade et al. [11].

Regarding the CIE Lab color parameters, the yogurt enriched with the crowberry extract only differs significantly ($p < 0.05$, Tukey test) in the L^* and b^* color parameters, that represents the luminosity and yellowness color of product, respectively. The food color is an important quality attribute that influences at first the buying action of the consumer. For this, it is crucial that the appearance of the new yogurt meets the intention

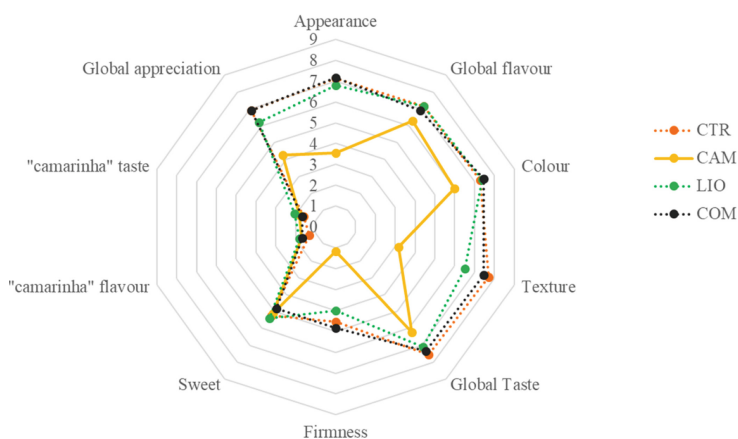
Table 1. Characterization of yogurt, manufactured with and without the crowberry fruits' extracts, regarding the pH-value, soluble solids content (SSC, °Brix) and color parameters (L*a*b*)

Quality attributes	CTR	LIO	CAM
pH	4.57 ± 0.01 ^a	4.57 ± 0.01 ^a	4.52 ± 0.02 ^a
SSC (°Brix)	16.41 ± 0.07 ^a	15.94 ± 0.05 ^b	16.57 ± 0.06 ^a
L*	87.70 ± 0.60 ^a	89.08 ± 0.41 ^c	82.23 ± 0.94 ^b
a*	-3.91 ± 0.06 ^a	-3.95 ± 0.08 ^a	-3.61 ± 0.28 ^b
b*	5.89 ± 0.62 ^a	8.33 ± 0.49 ^b	6.13 ± 1.33 ^a
TPC (mg GAE.g ⁻¹)	0.70 ± 0.31 ^a	1.27 ± 0.15 ^a	1.35 ± 0.06 ^b

The presented results denote the average ± standard deviation.

Different letters, in the same Line, represents significant difference at p-value < 0.05 (Tukey test).

of consumers, a pleasant overall appearance, as can be detected by the results obtained in the sensorial analysis (Fig. 4).

**Fig. 4.** Sensorial evaluation of the yogurt samples (with: LIO and CAM and without extract of the Portuguese white crowberry fruits: CTR and the commercial yogurt: COM).

The acceptability of a new food product from the consumer point of view is an important and major factor in the success of the product. By comparison of the enriched yogurt samples, a similar appearance with an identical color and global flavor was achieved in LIO and CTR samples. Despite the slight difference between the texture of this yogurt samples, in both a pleasant with a small difference in firmness was detected. As previously mentioned, the CAM yogurt sample did not achieve the expected solid texture and for this reason the panelists evaluated this enriched yogurt as low pleasant as compared to the other enriched yogurt samples.

4 Conclusions

The present study reveals the potential of unexploited and endemic wild crowberry fruits, showing the advantage of its use in the freeze-dried way as a natural and promising ingredient with health promoting compounds. Since the preliminary work showed the potential of the Portuguese white crowberry fruits, as a new ingredient in yogurt manufacturing, further studies regarding the evaluation of its bioactive composition such as the antioxidant capacity expressed by different methodologies as DPPH scavenging activity, ferric reduction activity potential and ABTS are in progress.

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References

1. Jacinto, J., Giovanetti, M., Oliveira, P.B., Valdivieso, T., Máguas, C., Alegria C.: Quality attributes of cultivated white crowberries (*Corema album* (L.) D. Don) from a multi-origin clonal field. *Euphytica* **217**(3), 40 (2021)
2. Bras De Oliveira, P., Dale, A.: *Corema album* (L.) D. Don, the white crowberry—a new crop. *J. Berry Res.* **2**, 123–133 (2012)
3. Ormonde, J., Constância, J.: Contributo para o conhecimento da Flora Vascular dos Açores. I: anotações e esclarecimentos relativos à Ilha do Pico., July 1992
4. Andrade, S.C., Guiné, R.P.F., Gonçalves, F.J.A.: Evaluation of phenolic compounds, antioxidant activity and bioaccessibility in white crowberry (*Corema album*). *J. Food Measur. Charact.* **11**(4), 1936–1946 (2017)
5. Brito, C., et al.: *Corema album* spp: Crowberries silvestres comestíveis com alto teor de minerais e ácidos orgânicos. *Food Chem.* **345**, 128732 (2021)
6. Andrade, S.C.: Estudo das propriedades físico químicas e avaliação de compostos bioativos em camarinhas, *Corema album* L. D. Don, *CAN THE CAN* (2016)
7. Pinheiro, J., Ganhão, R., Gonçalves, E.M., Silva, C.L.M.: Assessment of thermosonication as postharvest treatment applied on whole tomato fruits: optimization and validation. *Foods* **8**(12), 649 (2019)
8. Singleton, V.L., Rossi, J.A.: Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* **16**(3), 144–158 (1965)
9. Grasso, N., Alonso-Miravalles, L., O'Mahony, J.A.: Composition, Physicochemical and Sensorial Properties of Commercial Plant-Based Yogurts. *Foods* **9**, 252 (2020)
10. Lück, E., von Rymon Lipinski, G.: Foods, 3. Food Additives. In: *Ulmann's Encycl. Ind. Chem.*; Elvers, B., Ed., pp. 671–692. Wiley-VCH, Weinheim (2000)
11. Andrade, S.C., Gonçalves, F.J.A., Guiné, R.P.F.: Physical-chemical properties of *Corema album* (white crowberry or camarinha). In: *Proceedings of ICEUBI2015-International Conference of Engineering: Engineering for Society* (2015)



Catalytic Gasification of Coals and Biochars: A Brief Overview

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Abstract. Coal gasification is a mature technology for conversion of fossil coal to syngas and subsequently produce chemicals and fuels. In recent years, gasification has been proposed as a suitable technology for conversion of biomass and waste materials, to promote renewable energy sources and circular economy. Gasification of polymeric and miscellaneous wastes often requires a pre-carbonization step to obtain a homogeneous raw material with better fuel properties. However, coal and biochar gasification face specific challenges that require adequate solutions. These materials have high chemical stability and low volatile matter content, characteristics that hinder their full gasification at low temperature. Also, they may yield large fractions of tars and impurities that must be removed from the syngas before it can be used in energy or material applications. The use of catalysts can mitigate these limitations by reducing the activation energy of gasification. Alkali metal and alkaline-earth metal (AAEM), transition metal compounds and natural catalysts are the most widely used catalysts in the coal gasification process, due to their catalytic activity, availability, and low cost. Composite catalysts may allow a higher efficiency, as they have strong synergies, higher stabilities and can improve the gasification conversion rate compared to single catalysts. The scope of this review is the assessment of gasification fundamentals and technology, and the specific conditions for coal and biochar gasification. In addition, the authors comparatively discuss various catalyst typologies in gasification, and sheds light on low-cost and environmentally friendly catalysts as a potential solution for coal and biochar gasification.

Keywords: Coals · Biochars · Catalysts · Gasification

1 Introduction

1.1 Exploring Gasification

The history of gasification is not recent, the first real application was developed in 1798 by William Murdoch that proposed coal gasification to obtain a combustible gas, at the

time called town gas and that was used for lighting purposes. Various cities in Britain used town gas (also called coal-gas) for street lighting. From 1798 to 1850, the technology was improved, and several reactors were developed, but the invention of the electric bulb (after 1879) led to a significant decline of the town gas industry and gasification became confined to heating and cooking applications [1, 2]. Coal gasification regain interest during World War I and II, due to the scarcity of oil and refined fuels. The Fischer-Tropsch process to produce oil from syngas was proposed and used to obtain alternative liquid fuels [1]. Biomass gasification also became very popular during World War II, when approximately one million downdraft “gas producers” were used to power cars, trucks, boats, trains, and electric generators in Europe and in the United States [3]. After the war, interest in coal and biomass gasification technologies declined again due to the growing availability of cheap crude oil. The first commercial gasification plant (the Wabash River Coal Gasification Project) was implemented in 1999 in the USA [1, 2, 4]. The instability of fossil fuel prices (mainly oil), and concerns of climate change and environmental pollution, have put biomass and waste gasification increasingly under the spotlight, increasing the number of gasification projects around the world [4, 5]. Gasification is a key process for enabling the chemical utilization of carbonaceous resources to produce chemicals and fuels. The main application areas are: (1) chemical recycling of carbonaceous waste to replace fossil feedstock, (2) production of green hydrogen from (biogenic) waste, and (3) CO₂ neutral liquid fuels from biogenic wastes for transportation sectors [6]. The substitution of fossil fuels, such as coal, by biomass/biochar gasification is one of the current decarbonization strategies, allowing the capture of CO₂ or even negative CO₂ emissions [1].

2 Coal and Biochar Gasification: Main Limitations and Concerns

Gasification is the thermochemical conversion of organic solid material (coal, biomass, plastics, and organic waste) into a gaseous mixture of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and methane (CH₄) via partial oxidation. Is typically carried out at temperatures of 700–1500 °C and atmospheric pressure in the presence of pure oxygen, air, steam, and CO₂ [5, 7, 8]. Gasification is very sensitive to the nature of the feedstock, that strongly influences gasification performance and syngas composition [9]. Coal or biochar gasification at moderate temperatures (~700 °C), may lead to incomplete thermal decomposition given the high chemical stability of the raw materials. In those conditions it is expectable to occur the formation of tars and impurities that preclude direct use of syngas for power generation [10–12]. The efficient operation of engines coupled to gasification plants requires high-quality gas fuel [13], with CO and H₂ concentrations higher than 10% and a high calorific value very low tar content (<100 mg/Nm³) and total absence of particles, ammonia, and sulphur dioxides (NH₃, SO₂) [14, 15]. Tar compounds may condense in compressors and gas engines, restricting their technical and commercial viability [16]. Other impurities such as ammonia, acid compounds and ashes need to be completely removed, to ensure proper operation of the energy conversion equipment [13, 17]. The high ash content and mineral composition of coals and biochars can also lead to the formation of high levels of solid by-products and fly-ashes [18]. Increasing the gasification temperature can improve the carbon conversion efficiency of coals and biochars, but may also increase CO₂ production, reducing

the calorific value of the syngas [11, 12]. The use of catalysts seems to be an option to mitigate these limitations by reducing the activation energy and improving the reaction efficiency of gasification and facilitating tar cracking at lower temperatures [17, 19]. Catalysts ease the thermal and mass transfer resistance through the particles while providing an alternative lower-energy pathway for the reaction to proceed [4].

3 Investigating Common Catalyst in Coal and Biochar Gasification

Alkali and alkaline-earth metals (AAEM) such as potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg), and transition metal like iron (Fe), nickel (Ni), cobalt (Co) compounds, are the most frequent components of catalysts used for coal gasification [20, 21]. Sodium salts have been recognized to be excellent catalysts, which can accelerate gasification reaction rate and lower reaction temperature by 200–300 °C [22]. Most of these metals (Na, K and Ca) are already abundant in biochars therefore may act as natural catalysts, decreasing the cost of an added industrial catalyst [18]. The biochar reactivity in the gasification process is associated with structural features of char such as mineral content, porosity and surface area and active sites [23]. The AAEM'S that are inherently present in the biochar could also serve as catalytic active sites to induce tar reforming reactions [8]. However, the activity of aaem catalysts increases with increasing loading, so the number of catalytically active species contained in the biochar may not be sufficient. Therefore, increasing the number of active species by adding catalyst to the feed or to the gasification bed may be a more efficient solution [24].

3.1 Catalyst Classification: Single Component, Composite, and Disposable

Catalysts can be classified into single or composite materials, and reusable or disposable catalysts. In the case of single-component catalysts it has been shown that the catalytic activities of alkali metal are higher than those of alkaline earth metal and transition metal for three main gasification reactions [25]. For alkali catalyst the catalytic activity increases with the increase of relative atomic mass of alkali metal. For example, the order for catalytic activity of the alkali metal carbonates is $\text{Cs}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{Li}_2\text{CO}_3$. Due to the Cs high price, It is not suitable for industrial application, which makes k is the first choice, presenting a good catalytic activity and less tendency of coking. Catalysts containing K used in gasification are mostly k_2co_3 and koh which are compounds naturally found in biochar [26]. Apparent realizations of promoters can be obtained by combining catalysts. The combination of catalysts, results in Catalysts that may include binary composites or ternary composites. The K catalytic effect can be influenced by the presence of Ca, so positive synergic effects can be obtained when combining K and Ca catalysts. Several roles of ca had been verified during the gasification, such as promoting the gasification rate, protecting potassium avoiding deactivation, sulfur fixation, and *in-situ* carbon dioxide capture [20, 25, 26]. The steam gasification of corn cob biochar was evaluated using four alkali salts as catalysts (KOH, K_2CO_3 , NaOH and Na_2CO_3) and the highest catalytic activity was obtained for alkali hydroxides. The maximum H_2 yield of 197.8 g/kg coal was obtained with 6%wt KOH [12]. Karimi *et al.*, (2011) reported that K_2CO_3 and Na_2CO_3 were the most effective catalysts for bitumen

coke steam gasification at 600–800 °C. When K_2CO_3 , KCl, Na_2CO_3 , $CaCO_3$, CaO and MgO are selected as catalysts [27]. Indeed, alkaline carbonates and hydroxides relatively have greatest catalytic activity compared with metal sulfates, nitrates, oxides, and acetates [20, 25, 26]. Other studies proved that composite catalysts (Na_2CO_3 - $FeCO_3$) have better catalytic activity than individual catalysts during coal gasification with CO_2 . They have strong synergy, higher stability and can increase the gasification conversion rate by 100–500% compared to the effect of individual Na_2CO_3 and Fe_2CO_3 -based catalysts [20]. However, composite catalysts, especially ternary ones, are very difficult to recover. on the other hand, disposable catalysts are cheap catalysts, usually corresponding to residues from agriculture, forestry, and industry, existing in abundance and widely available. They are economically and environmentally friendly catalysts. nevertheless, their catalytic activities are often low [25]. The comparisons of different types of catalysts are shown below in Table 1.

Table 1. Comparison of different types of catalysts. Adapted from [25].

Parameter	Alkali metal	Alkaline earth metal	Transition metal	Composite catalysts	Disposable catalysts
Representative	K	Ca	Fe	K-Na-Li	Biomass ash
Catalytic loading amount	Large	Medium	Small	Large	Small
Recovery	Difficult	-	-	Very difficult	No
Price	High	Low	Low	Medium	Very low
Activity	High	Medium	Medium	Very high	Low

Numerous studies on the catalytic gasification of coals and biochars with single, composite, and disposable catalytic species have been performed and are discussed in the next sections.

4 Investigating Catalysts for Tar Removal and Syngas Improvement in Coal and Biochar Gasification

Most of the work for tar minimization has been done in catalytic cracking of the tar because of the multiple advantages of catalytic degradation compared to the alternatives like mechanical method such as dry gas cleaning and wet gas cleaning, thermal cracking, and plasma method. Catalysts can degrade comparatively stable compounds such as aromatics and polycyclic aromatic hydrocarbon (PAHs). They can be employed *in-situ* during the gasification reactions or *ex-situ* after gasification reactions for tar removal and syngas quality improvement [4]. *In situ* gas cleaning (primary measures) involves incorporating or mixing catalyst with the feed or by the utilization of catalytically active bed material to achieve catalytic gasification [28]. *In situ* measures are attractive since they reduce the need for downstream cleaning equipment, and the energy content of the

undesirable species is retained in the product gas. Generally, naturally occurring minerals such as dolomite, limestone, bauxite, and olivine are utilized as the bed materials owing to their higher catalytic activities [29]. Some these catalytically active bed materials such as, olivine and bauxite are suitable options for adjusting the H_2/CO inside the gasifier, promote water-gas-shift reactions (WGS) and gas quality [29, 30]. The *ex-situ* gas cleaning strategies (secondary measures) use an additional reactor down-stream the gasifier to remove or convert the tar. It includes catalytic cracking with active bed material as used in the *in-situ* gas cleaning strategies. Catalytic tar removal takes place at a comparatively lower range of temperature 700–900 °C when compared to regular thermal processes (1100–1300 °C) [29]. *In-situ* catalysts are the most suitable and effective strategy for tar catalytic removal and H_2 -rich gas production by reducing tar formation and enhancing the tar reforming into useful product gas [28]. For tar cracking, the most applied catalysts are nickel-based. Ni is characterized by high catalytic activity for the reformation reactions but its resistance to sulphur poisoning, sintering and carbon deposition strongly depends on the support material, promoters and other additives that are utilized in its manufacture. Also, they require cheap carbon sorbents to have a profound effect [4]. To date, potassium carbonate (K_2CO_3) has been the most suitable for catalytic gasification of industrialized coal. The K-Ca composite catalyst is a promising catalyst due to high gasification rate, CO_2 and H_2S capture removal, but is difficult to recover [25]. The main catalysts used in removing tar and promoting H_2 production from the syngas of catalytic gasification of coal and biochar are presented below in Table 2.

Table 2. Catalysts used in tar removing and H_2 production during coal and biochar gasification.

Feed	Atmosphere	Catalyst	Tar content (g/Nm ³)	H_2 content (vol.%)	Reference
Bitumen coke	Steam	K_2CO_3	-	68.3 (mol.%)	[27]
		Na_2CO_3	-	71.5 (mol.%)	
Yuyang coal	Steam	Alkali-feldspar and Quartz sand (bed material)	10.2	57.1	[29]
		Quartz sand (bed material)	55.5	47.9	
Bituminous coal	Steam	Calcined olivine (bed material)	16.8	50.9	[31]
Bituminous coal	Steam	Na^+ (1 wt%)	-	62.0	[24]
50% Brown coal + 50% pine sawdust	Steam	Calcined dolomite (bed material)	7.2	50.6	[32]

(continued)

Table 2. (continued)

Feed	Atmosphere	Catalyst	Tar content (g/Nm ³)	H ₂ content (vol.%)	Reference
		Olivine (bed material)	9.1	47.2	
		Sand (bed material)	16.4	38.1	
Sawdust biochar	Steam	KCe (5%K + 5%Ce)	-	67.6	[33]
		KCo (5%K + 5%Co)	-	65.4	
Sub-bituminous coal	Steam	Chicken calcined eggshell (20wt%)	-	64.0	[34]
Anthracite coal	Steam	Spirit-based distillers' grains (1:1)	-	68.0	[35]
80%coal + 20%polyethylene	Steam/O ₂	Ni-dolomite	13.0	31.0	[36]
Bituminous coal + wood residue	O ₂	K ₂ CO ₃ (mass ratio 1.0)	9.62	52.05	[37]
60% sub-bituminous coal + 40% sawdust	Air	Silica sand (bed material)	5.61 (g/kg)	11.0	[38]
Lignite	Air	Quartz sand (bed material)	0.365	8.3	[39]
Turkish coal (25.62 wt% ash)	Air	Calcined dolomite (10wt%)	-	17.70	[40]
Bituminous coal	Air	Calcined dolomite (5wt%)	25.2 (g/kg)	-	[41]
70%Coconut shell + 30%Biochar	Air	Biochar (30wt%)	-	8.84	[42]

Although many types of catalysts can catalyze tar upgrading and improve syngas quality during gasification, some disadvantages may limit their industrial application. The high cost of the catalyst materials themselves, the decline in their performance and activity over time, and the difficulty in recovering and recycling some catalysts, triggers the search for efficient, cost-free, and highly stocked waste materials as gasification catalysts [43]. The search for environmentally friendly catalysts in coal and biochar gasification is a current goal to make these processes cost competitive in the markets.

Studies have been done in this direction. For example, Fan *et al.*, (2017), used calcined chicken eggshell as a catalyst in the steam gasification of sub-bituminous coal in a tubular fixed bed. The results showed that compared to the raw coal non-catalytic gasification, the use of calcined eggshell could improve the carbon conversion, reaction rate and yield of H₂ (80% higher) in the syngas [34]. Lv *et al.*, (2019), in steam gasification of blends of anthracite coal using spirit-based distillers' grains as a catalyst with mass ratios of 1:1, also recorded an increase in H₂ concentration compared to not using a catalyst [35]. Development on known catalysts and work on new and more innovative and suitable catalysts are promising options to minimize tar and improve syngas quality.

5 Conclusion

Gasification is a key process for enabling the chemical utilization of carbonaceous resources to produce chemicals and fuels. Coal or biochar gasification has some specific challenges such as the high ash content and mineral composition of these materials as well as the significant amounts of produced tars that must be removed from the syngas. The use of catalysts seems to be an option to mitigate these limitations. Most studies of catalytic gasification of coal and biochar use steam as the reaction medium, which ultimately favors hydrogen production. The use of air despite decreasing the costs of the process seems to have received little attention. Natural catalysts such as dolomite, olivine and quartz sand and composite catalysts (essentially carbonate catalysts) are the most used in catalytic gasification of coal and biochar, showing good catalytic activity in reducing tar and promoting H₂ production. More disposable waste catalysts with acceptable catalytic activities need to be developed to make these processes cost competitive. Catalytic gasification of coal and biochar can potentially become a widely used process on an industrial scale if the catalysts selected are cheap and efficient.

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References

1. Pio, D.T., Tarelho, L.A.C.: Industrial gasification systems (>3 MWth) for bioenergy in Europe: current status and future perspectives. *Renew. Sustain. Energy Rev.* **145** (2021). Elsevier Ltd. <https://doi.org/10.1016/j.rser.2021.111108>
2. Singh Siwal, S., Zhang, Q., Sun, C., Thakur, S., Kumar Gupta, V., Kumar Thakur, V.: Energy production from steam gasification processes and parameters that contemplate in biomass gasifier – a review. *Bioresour. Technol.* **297** (2020). <https://doi.org/10.1016/j.biortech.2019.122481>
3. Indrawan, N., Kumar, A., Moliere, M., Sallam, K.A., Huhnke, R.L.: Distributed power generation via gasification of biomass and municipal solid waste: a review. *J. Energy Inst.* **93**(6) (2020). <https://doi.org/10.1016/j.joei.2020.07.001>









4. Sikarwar, V.S., et al.: An overview of advances in biomass gasification. *Energy Environ. Sci.* **9**(10), 2939–2977. Royal Society of Chemistry, 01 October 2016. <https://doi.org/10.1039/c6e00935b>
5. Umenweke, G.C., Afolabi, I.C., Epelle, E.I., Okolie, J.A.: Machine learning methods for modeling conventional and hydrothermal gasification of waste biomass: a review. *Bioresour. Technol. Reports* **17**, 01 February 2022. Elsevier Ltd. <https://doi.org/10.1016/j.biteb.2022.100976>
6. Lee, R.P., Seidl, L.G., Huang, Q.L., Meyer, B.: An analysis of waste gasification and its contribution to China's transition towards carbon neutrality and zero waste cities. *Ranliao Huaxue Xuebao/J. Fuel Chem. Technol.* **49**(8) (2021). [https://doi.org/10.1016/S1872-5813\(21\)60093-2](https://doi.org/10.1016/S1872-5813(21)60093-2)
7. Dogu, O., et al.: The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: state-of-the-art, challenges, and future directions. *Progress Energy Combust. Sci.* **84** (2021). <https://doi.org/10.1016/j.peccs.2020.100901>
8. Yang, Y., et al.: Gasification of refuse-derived fuel from municipal solid waste for energy production: a review. *Environ. Chem. Lett.* **19**(3), 2127–2140 (2021). <https://doi.org/10.1007/s10311-020-01177-5>
9. Ramos, A., Monteiro, E., Silva, V., Rouboa, A.: Co-gasification and recent developments on waste-to-energy conversion: a review. *Renew. Sustain. Energy Rev.* **81**, 380–398, March 2017 (2018). <https://doi.org/10.1016/j.rser.2017.07.025>
10. Segurado, R., Pereira, S., Correia, D., Costa, M.: Techno-economic analysis of a trigeneration system based on biomass gasification. *Renew. Sustain. Energy Rev.* **103**, pp. 501–514, January 2018 (2019). <https://doi.org/10.1016/j.rser.2019.01.008>
11. Ge, Z., Guo, L., Jin, H.: Catalytic supercritical water gasification mechanism of coal. *Int. J. Hydrogen Energy* **45**(16) (2020). <https://doi.org/10.1016/j.ijhydene.2020.01.245>
12. Ning, S., Jia, S., Ying, H., Sun, Y., Xu, W., Yin, H.: Hydrogen-rich syngas produced by catalytic steam gasification of corncob char. *Biomass Bioenergy* **117** (2018). <https://doi.org/10.1016/j.biombioe.2018.07.003>
13. Molino, A., Chianese, S., Musmarra, D.: Biomass gasification technology: the state of the art overview. *J. Energy Chem.* **25**(1), 10–25 (2016). <https://doi.org/10.1016/j.jechem.2015.11.005>
14. Sansaniwal, S.K., Rosen, M.A., Tyagi, S.K.: Global challenges in the sustainable development of biomass gasification : an overview. *Renew. Sustain. Energy Rev.* **80**, 23–43 (2017). <https://doi.org/10.1016/j.rser.2017.05.215>
15. Vaish, B., Sharma, B., Srivastava, V., Singh, P., Ibrahim, M.H., Singh, R.P.: Energy recovery potential and environmental impact of gasification for municipal solid waste. *Biofuels* **10**(1), 87–100 (2019). <https://doi.org/10.1080/17597269.2017.1368061>
16. Watson, J., Zhang, Y., Si, B., Chen, W., de Souza, R.: Gasi fi cation of biowaste : a critical review and outlooks. 83, 1–17, August 2017 (2018). <https://doi.org/10.1016/j.rser.2017.10.003>
17. Ruiz, J.A., Juárez, M.C., Morales, M.P., Muñoz, P., Mendivil, M.A.: Biomass gasification for electricity generation: review of current technology barriers. *Renew. Sustain. Energy Rev.* **18**, 174–183 (2013). <https://doi.org/10.1016/j.rser.2012.10.021>
18. Wei, J., Gong, Y., Guo, Q., Chen, X., Ding, L., Yu, G.: A mechanism investigation of synergy behaviour variations during blended char co-gasification of biomass and different rank coals. *Renew. Energy* **131** (2019). <https://doi.org/10.1016/j.renene.2018.07.075>
19. Yang, F., Yu, Q., Duan, W., Qi, Z., Qin, Q.: Electrochemical catalytic coal gasification: a novel method. *Catalysis Commun.* **150** (2021). <https://doi.org/10.1016/j.catcom.2020.106261>
20. Xu, B., et al.: Kinetics and mechanism of CO₂ gasification of coal catalyzed by Na₂CO₃, FeCO₃ and Na₂CO₃–FeCO₃. *J. Energy Inst.* **93**(3) (2020). <https://doi.org/10.1016/j.joei.2019.08.004>

21. Lu, G., et al.: Changes in active sites and reactivity induced by interactions among Ca, Si and Al during coal char gasification. *Fuel* **310** (2022). <https://doi.org/10.1016/j.fuel.2021.122322>
22. Han, L., et al.: In-situ catalytic gasification of sodium-rich direct coal liquefaction residue under CO₂ atmosphere and kinetic analysis of gasification reaction process. *J. Energy Inst.* **101**, 233–242 (Apr.2022). <https://doi.org/10.1016/j.joei.2022.02.002>
23. Abdalazeez, A., Li, T., Wang, W., Abuelgasim, S.: A brief review of CO₂ utilization for alkali carbonate gasification and biomass/coal co-gasification: reactivity, products and process. *J. CO₂ Utilization* **43** (2021). <https://doi.org/10.1016/j.jcou.2020.101370>
24. Zubek, K., Czerski, G., Porada, S.: Determination of optimal temperature and amount of catalysts based on alkali and alkaline earth metals for steam gasification process of bituminous coal. *Thermochimica Acta* **665** (2018). <https://doi.org/10.1016/j.tca.2018.05.006>
25. Li, W., Yu, Z., Guan, G.: Catalytic coal gasification for methane production: a review. *Carbon Resour. Convers.* **4** (2021). <https://doi.org/10.1016/j.crcon.2021.02.001>
26. Dahou, T., Defoort, F., Khiari, B., Labaki, M., Dupont, C., Jeguirim, M.: Role of inorganics on the biomass char gasification reactivity: a review involving reaction mechanisms and kinetics models. *Renew. Sustain. Energy Rev.* **135** (2021). <https://doi.org/10.1016/j.rser.2020.110136>
27. Karimi, A., Gray, M.R.: Effectiveness and mobility of catalysts for gasification of bitumen coke. *Fuel* **90**(1) (2011). <https://doi.org/10.1016/j.fuel.2010.07.032>
28. Shen, Y., Yoshikawa, K.: Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis - a review. *Renew. Sustain. Energy Rev.* **21** (2013). <https://doi.org/10.1016/j.rser.2012.12.062>
29. Khan, M.M., Xu, S., Wang, C.: Catalytic gasification of coal in a decoupled dual loop gasification system over alkali-feldspar. *J. Energy Inst.* **98** (2021). <https://doi.org/10.1016/j.joei.2021.06.003>
30. Berdugo Vilches, T., Marinkovic, J., Seemann, M., Thunman, H.: Comparing active bed materials in a dual fluidized bed biomass gasifier: olivine, bauxite, quartz-sand, and ilmenite. *Energy and Fuels* **30**(6), 4848–4857 (2016). <https://doi.org/10.1021/acs.energyfuels.6b00327>
31. Xiao, Y., Xu, S., Song, Y., Wang, C., Ouyang, S.: Gasification of low-rank coal for hydrogen-rich gas production in a dual loop gasification system. *Fuel Process. Technol.* **171** (2018). <https://doi.org/10.1016/j.fuproc.2017.11.014>
32. Ma, X., Zhao, X., Gu, J., Shi, J.: Co-gasification of coal and biomass blends using dolomite and olivine as catalysts. *Renewable Energy* **132**, 509–514 (2019). <https://doi.org/10.1016/j.renene.2018.07.077>
33. Jiao, W., et al.: Catalytic steam gasification of sawdust char on K-based composite catalyst at high pressure and low temperature. *Chem. Eng. Sci.* **205**, 341–349 (2019). <https://doi.org/10.1016/j.ces.2019.05.009>
34. Fan, S., Xu, L.H., Kang, T.J., Kim, H.T.: Application of eggshell as catalyst for low rank coal gasification: experimental and kinetic studies. *J. Energy Inst.* **90**(5) (2017). <https://doi.org/10.1016/j.joei.2016.07.008>
35. Lv, J., Ao, X., Li, Q., Cao, Y., Chen, Q., Xie, Y.: Steam co-gasification of different ratios of spirit-based distillers' grains and anthracite coal to produce hydrogen-rich gas. *Bioresour. Technol.* **283** (2019). <https://doi.org/10.1016/j.biortech.2019.03.047>
36. Pinto, F., Lopes, H., André, R.N., Gulyurtlu, I., Cabrita, I.: Effect of catalysts in the quality of syngas and by-products obtained by co-gasification of coal and wastes. 1. Tars and nitrogen compounds abatement. *Fuel* **86**(14) SPEC. ISS., 2052–2063 (2007). <https://doi.org/10.1016/j.fuel.2007.01.019>
37. Peng, W.X., Ge, S.B., Ebadi, A.G., Hisoriev, H., Esfahani, M.J.: Syngas production by catalytic co-gasification of coal-biomass blends in a circulating fluidized bed gasifier. *J. Cleaner Prod.* **168** (2017). <https://doi.org/10.1016/j.jclepro.2017.06.233>

38. Mallick, D., Mahanta, P., Moholkar, V.S.: Co-gasification of coal/biomass blends in 50 kW circulating fluidized bed gasifier. *J. Energy Inst.* **93**(1), 99–111 (2020). <https://doi.org/10.1016/j.joei.2019.04.005>
39. Zeng, X., Wang, F., Han, Z., Sun, Y., Cui, Y., Xu, G.: Characterization and pilot scale test of a fluidized bed two-stage gasification process for the production of clean industrial fuel gas from low-rank coal. *Carbon Resources Conversion* **1**(1) (2018). <https://doi.org/10.1016/j.crcon.2018.05.003>
40. Karatas, H., Olgun, H., Akgun, F.: Coal and coal and calcined dolomite gasification experiments in a bubbling fluidized bed gasifier under air atmosphere. *Fuel Process. Tech.* **106** (2013). <https://doi.org/10.1016/j.fuproc.2012.09.063>
41. Sciazko, M., Kubica, K.: The effect of dolomite addition on sulphur, chlorine and hydrocarbons distribution in a fluid-bed mild gasification of coal. *Fuel Process. Technol.* **77–78** (2002). [https://doi.org/10.1016/S0378-3820\(02\)00060-7](https://doi.org/10.1016/S0378-3820(02)00060-7)
42. Monir, M.U., Abd Aziz, A., Kristanti, R.A., Yousuf, A.: Gasification of lignocellulosic biomass to produce syngas in a 50 kW downdraft reactor. *Biomass Bioenergy* **119** (2018). <https://doi.org/10.1016/j.biombioe.2018.10.006>
43. Chen, Z., et al.: Novel application of red mud as disposal catalyst for pyrolysis and gasification of coal. *Carbon Resour. Convers.* **4** (2021). <https://doi.org/10.1016/j.crcon.2021.01.001>



The Influence of Fuel Mix on the Devolatilization of RDF Based Coal

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Abstract. Thermochemical conversion of solid fuels depends on the devolatilization rate of the volatile compounds. Depending on the process, the temperature is the key variable that controls such a process. Refuse Derived Fuels (RDFs) are fuels that can have a positive impact on the energy mix while contributing to the reduction of landfill material. Due to its variable composition, to design the conversion facility, it is of utmost relevance to have an accurate understanding of the actual behaviour of the fuel. Although gasification is the preferred route for energy conversion of RDF, carbonization appears to be an attractive pre-treatment process to reduce the corrosive compounds such as chloride RDF. For this purpose, samples were selected from a waste treatment plant in the north of Portugal, and the char was obtained after 30 min carbonization at 400 °C. Vegetable char was also tested to be used as the main reference. To understand the influence of other materials on the process, biomass and sewage sludge were used. Mixed with the RDF char on a weight percentage of 20%. The thermal degradation was performed on an oven, equipped with an oxidant agent inlet, a scale, and a gas collecting system to analyse the combustion gases. To complement the data, a TGA and DSC analysis were also performed in both air and argon atmosphere. The data demonstrates that the vegetable char presents the highest resistance to thermal degradation, followed by the RDF char, the RDF char with SS, and the RDF char with biomass.

Keywords: RDF · Char · Devolatilization · Fuel Mix · Carbonization · Biomass · Sewage Sludge

1 Introduction

Refuse Derived Fuels (RDF) are wastes originated from the treatment of Municipal Solid Wastes (MSW). Because of their main composition, they are considered fuels and

they can be used for power generation on a power facility. These power facilities can operate on different types of process. They can operate as direct combustion, or even as a gasification or pyrolysis process.

In Portugal it was reported that, in 2019, 683 t of RDF were produced [1]. However, not all this amount was used for power generation. The RDF has a major problem, sometimes, their heterogeneity and composition (mostly, moisture and chlorine content) makes it unsuitable to use it as a fuel. In that case, the only option is sent it to landfill. As a solution, the carbonization appears as a pre-treatment process to uniformize the product and make it reliable for power generation. Reducing the moisture and chlorine content, and increasing the Low Heating Value and carbon percentage of the fuel [2].

However, being the RDF a waste with a wide versatility in composition, the char itself will also present some versatility. So, it is important on a first stage understand the devolatilization process of the material in order to design a proper facility. Assess the best conditions to use the material as a fuel or even understand if any additives are necessary [3].

In that sense, thermal degradation, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) can provide fundamental information concerning the temperature range for maximum weight loss, reaction rate, and devolatilization gas composition [4].

Several authors have performed this type of analysis and proved to be relevant for their work. Among them are Mohalik et al. [5] that applied this analysis to determine spontaneous combustion propensity behaviour of several types of coal; Chen et al. [6] that applied the TGA analysis to investigate the pyrolysis characteristics of several biomass; and Kim et al. [7] that have studied the physicochemical properties and pyrolysis kinetics of hazelnut husk.

The goal of this analysis is to provide some relevant data about the present RDF char to use it as a fuel on a future facility. Being relevant not only for academic but also for industrial purposes.

2 Materials and Methods

The experimental tests were performed using RDF Char (RDFc) obtained from an RDF carbonization performed under 400 °C during 30 min. The RDF was collected from a waste treatment power plant in the north of Portugal. Originated from hard wood, the vegetable char used as reference came from a certificated company. The sewage sludge (SS) came from a wastewater treatment plant in centre of Portugal and pine wood was used as biomass (Bio). The characterization of these materials was performed, and the results are depicted in Table 1.

Table 1. Properties of the different materials.

Analysis	SS	Bio	RDFc	VEGc
Proximate (dry basis)				
Moisture	10.0	9.5	2.4	5.4
Volatile Matter (VM)	58.6	91.6	61.7	21.2
Ash	37.3	0.1	25.5	6.1
Fixed Carbon (FC)	4.1	8.2	12.8	72.7
Ultimate (dry basis)				
Carbon (C)	33.1	50.4	58.3	77.8
Hydrogen (H)	4.5	6.4	5.6	2.7
Nitrogen (N)	3.5	0.1	1.6	0.6
Oxygen (O)	21.6	43.0	9.0	12.8

The Fixed Carbon and Oxygen were obtained by calculation, using the previous values. The fixed carbon was calculated following the Eq. (1):

$$\%FC = 100\% - \%Ash - \%VM \quad (1)$$

The Oxygen was calculated following the Eq. (2).

$$\%O = 100\% - \%Ash - \%C - \%H - \%N \quad (2)$$

2.1 Experimental Setup

The experimental tests were performed at the Heat and Fluids Laboratory of the Department of Mechanical Engineering of University of Minho. An oven, with a 5 L chamber, was adapted by a research team to implement a scale along with a gas inlet and a gas collecting system. The oven is capable of reach 1200 °C and has a Eurotherm Nanodac as a temperature controller.

The scale is a Shinko Denshi AJ-620CE with a capacity of 620 g, a readability and repeatability of 0.001 g. To control the air injected into the oven, a TSI 4043 Flow Meter was used. LabView was used as a software to acquire data from the scale and the flow meter sensor. To collect the devolatilization gases, a purpose made probe connected to a SKC 24-44MTX vacuum pump were used. The gas was collected into gas sample bags and then analysed.

The Thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) analysis were performed on a SDT 2960 Simultaneous DSC-TGA equipment from TA Instruments. To understand the influence of the atmosphere on the process, all samples were tested under air and argon atmosphere.

2.2 Test Procedure

The purpose of the tests is to study the devolatilization of the samples along time, under a controlled temperature. For that reason, no air was injected, and the air considered on the combustion process was the one presented on the oven, represented by its volume (≈ 5 L). The main sample to study is the RDF Char. The Vegetable char was implemented as a reference (common char on the market) and to understand the influence of another materials, SS and Biomass were also used. All the samples were weighted and mixed before entering the oven. For each test 30 g of sample were used. When the SS and Bio were added, these materials were mixed with the RDFc on a weight percentage of 20% (6 g of SS or Bio and 24 g of RDFc). To uniformize the tests, all the samples were sieved to have a particle diameter $< 500 \mu\text{m}$. To perform the tests, the oven was firstly pre-heated to 800°C . After the oven's temperature stabilization, the sample was introduced into the sample container, which is connected to the scale, and afterwards introduced inside the oven. The gases were stored into sample bags and then analysed in different parameters (H_2 , CO , CO_2 , CH_4 , O_2 and N_2). The gas sample was collected for 5 min starting from 1 min after the introduction of the sample in the oven.

For the DSC-TGA tests, once the amount of sample used in this type of tests are inferior to 10 mg, it is important to assure an uniformization of the sample. To minimize errors, particle diameter was reduced to $< 150 \mu\text{m}$. The sample was introduced into the equipment and heated up to 900°C on a heating rate of $10^\circ\text{C}/\text{min}$.

3 Results and Discussion

This chapter depicts the results obtained on the thermal degradation for the mass loss and devolatilization gas composition; and the DSC-TGA analysis of the four samples in both air and argon atmosphere.

3.1 Thermal Degradation

From all the samples, it is noticeable that the VEGc it the most resistant to thermal degradation (Fig. 1). Although the degradation curve is similar to the samples with RDFc, the reaction rate will be different. On the literature, the authors relate this event to the sample's composition. Explaining the higher thermal resistance due to the higher fixed carbon and lower volatile matter [8–10].

The samples with RDFc presented a similar behaviour between them. However, the incorporation of SS or Bio stands out as a major contribute to the sample's devolatilization. Specially for the Bio once was the additive that most contributed for the devolatilization process. This can be explained by the higher volatile matter of the biomass. Which contributes for a better reaction under this circumstances [11].

The overall mass loss percentage was 60% for RDFc with Bio, followed by 55% for the RDFc with SS, 52% for the RDFc, and 36% for the VEGc.

The gas analysis is representative of the phenomena that was demonstrated before. For the VEGc, the gas analysis (Table 2), shows a lack of diversity of gas products. Suggesting that there was a slight combustion, and the rest of the gas was air (present in the oven).

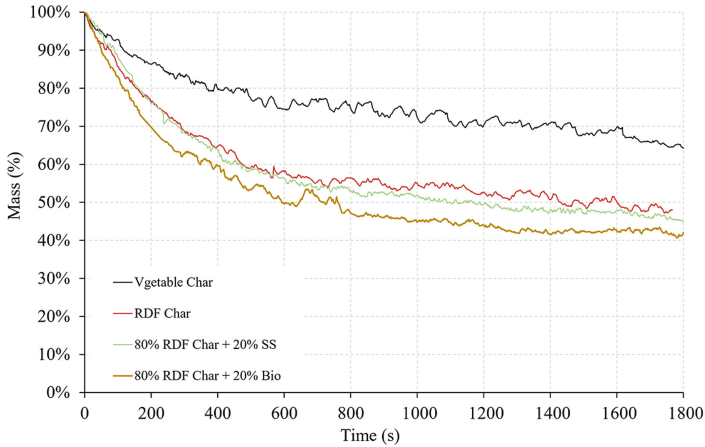


Fig. 1. Thermal degradation at 800 °C

Table 2. Gas analysis from the thermal degradation tests

Parameter (%)	RDFc + Bio	RDFc + SS	RDFc	VEGc
H ₂	1.5	2.7	3.6	0
O ₂	14.9	3.8	5.9	10.0
N ₂	70.5	69.4	70.2	78.1
CO	1.5	2.9	4.0	0
CH ₄	1.4	2.8	4.0	0
CO ₂	4.7	14.7	13.9	12.5

For the samples with RDFc the scenario was different. The air contained in the oven was the only available for reaction. However, was enough to produce some combustible gases. The RDFc with Bio was, among the three, the one with lower gas combustibles. The highest O₂% on the gas ($\approx 15\%$) suggest that this might be related to the composition of the Bio once it is the one with higher O% in its composition. The difference between the RDFc and RDFc with SS was subtle. However, the gas from the RDFc was slightly rich in combustible compounds. The higher CO₂ with SS imply that this additive emphasises combustion. Which can be a major contribute depending on the application. Despite its $\approx 14\%$ of CO₂, the RDFc gas was the one with higher H₂, CO and CH₄, suggesting that it is the most indicated for pyrolysis and gasification purpose.

3.2 TGA and DSC

3.2.1 Air Conditions

The TGA in air conditions (Fig. 2) comes to complement the information provided before. VEGc was the one that presented the highest ignition temperature. This phenomena is preferable to avoid spontaneous ignition, making the fuel storage and transportation safer [10]. It is noticeable that, till 200 °C, the RDFc was the one with the lowest mass loss. Being this the drying stage, the samples with lower moisture content will be the ones that will lose less mass until they reach the ignition point [12].

Although it is the one with higher ignition temperature, the almost vertical curve of VEGc mass loss implies that it is the one with higher reaction rate. Meaning that, even if the sample present less volatile matter compared to the other ones, the higher percentage of carbon will eventually be used to react with the available oxygen. While the other samples have more volatile matter but low carbon to react with the oxygen [12]. As a prove, Fig. 3 shows the DSC curve for the different samples. As it is depicted, the VEGc is the one presenting the highest peak, meaning the highest reaction rate of all. The max mass loss for the samples were, 89%, 84%, 81% and 78% for the VEGc, RDFc with Bio, RDFc with SS and RDFc, respectively.

As it was noticed before on the thermal degradation, the RDFc was the one that presented less reaction, followed by the RDFc with SS and Bio. Proving once again the importance of these additives for thermal degradation.

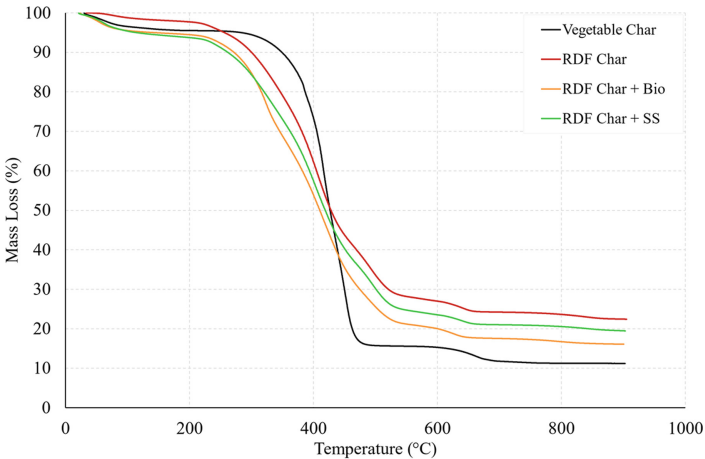


Fig. 2. TGA performed in Air Conditions

From the Fig. 3 it is noticed that there are two main peaks going on. The first major peaks developed are due to the combustion of volatile matter. The second major peaks triggered are owing to the combustion of remaining lignin and char or fixed carbon [8]. Otherwise, once the RDF is mainly composed by several materials, these two peaks could suggest there is two types of chars on the mixture. Further test should be performed to confirm this quote.

From the data it was possible to conclude that the VEGc was the one with highest heat flow, followed by RDFc with Bio, RDFc, and RDFc with SS. The values were 77, 21, 19, and 18 W/g, respectively.

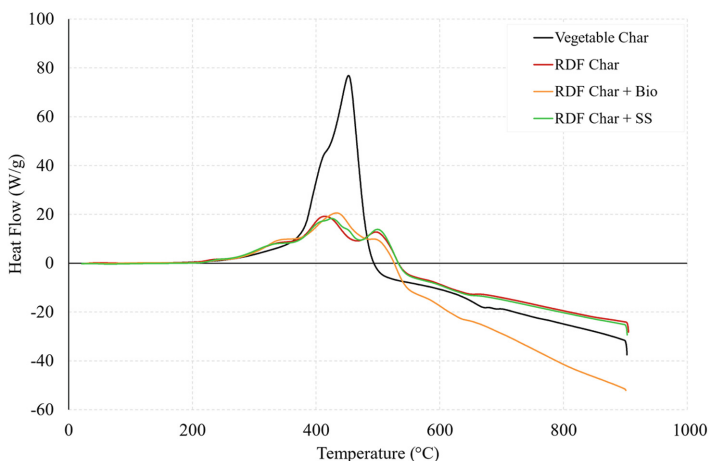


Fig. 3. DSC performed in Air Conditions

3.2.2 Argon Conditions

The TGA performed in argon conditions is similar to the thermal degradation showed previously. However, shall not be compared directly once the test conditions are not the same. For this case, the max mass loss obtained was 25%, 52%, 52% and 57% for the VEGc, RDFc, RDFc with SS and RDFc with Bio, respectively (Fig. 4). Once again, the VEGc in an atmosphere without oxygen has no way to react the internal carbon due to the lack of volatile matter. In contrast, the volatile matter presented on the other samples played a significant role for the reaction as a pyrolysis process [13]. As it can be noticed, the thermal degradation happens in several steps. These steps are the different stages of the pyrolysis process, which may occur in different stages of temperatures. This results are agreed with the literature [14].

Compared with the exothermic behaviour presented in atmospheric condition (positive part of the DSC graph), the main reactions are endothermic in argon atmosphere (negative part of the DSC graph) [15, 16]. In this scenario, the max heat flow released by the samples were, 0.346, 0.289, 0.286, and 0.243 W/g for RDFc with Bio, RDFc, VEGc and RDFc with SS, respectively. On the endothermic range (negative part of Fig. 5), the VEGc was the one that resisted the most to the temperature. For the RDFc and additives, the addition of Bio showed a beneficial behaviour, and the SS having the opposite effect. Having the RDFc in between the two additives.

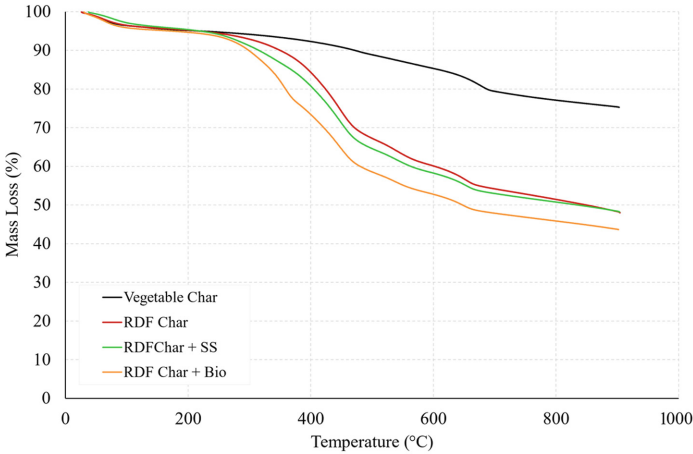


Fig. 4. TGA performed in Argon Conditions

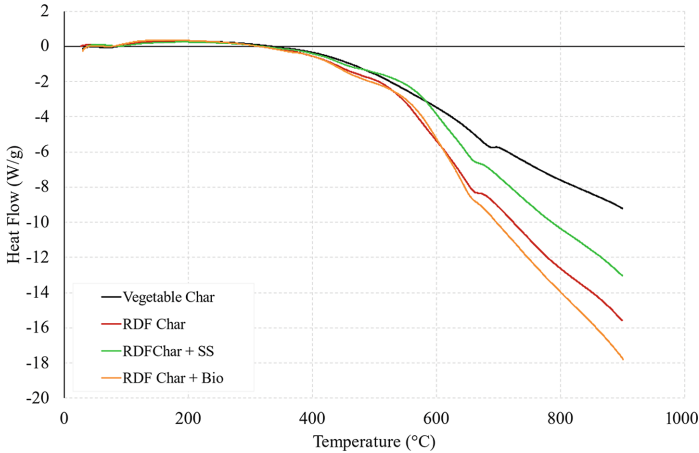


Fig. 5. DSC performed in Argon Conditions

4 Conclusions

The devolatilization of an RDF char were studied by performing a thermal degradation, TGA and DSC analysis. The RDFc was obtained from an RDF carbonization at 400 °C during 30 min. To complement the information, Vegetable char (VEGc) was used as reference and Biomass (Bio) and Sewage Sludge (SS) were used as additives to the RDFc, individually, on a mass percentage of 20%.

The thermal degradation occurred on an oven, at 800 °C and the gas from the devolatilization process was analysed. From the tests, the VEGc was the one that presented the most resistance for devolatilize, followed by the RDFc, RDFc with SS and RDFc with Bio. In this scenario, the addition of Bio provided conditions for a better

devolatilization rate. From the gas analysis, the RDFc proved to have the devolatilization gas with better quality for pyrolysis and gasification purposes.

On the DSC- TGA in air conditions, the VEGc proved to be the material with higher ignition temperature and higher reaction rate. Considered the most preferable for combustion purpose. Regarding the RDFc, the supplements proved to have a positive influence on the devolatilization process. Being the Bio, once more, the one with highest impact due to its higher volatile matter.

For the DSC- TGA in argon conditions, the VEGc showed same behaviour as in the thermal degradation tests. Being the one with the highest resistance to temperature. Regarding the other materials, the presence of Bio proved, a positive influence for the degradation process. However, the SS had the opposite behaviour, comparing with the RDFc without additives.

These types of analysis help to understand the behaviour of these materials and provide data in case of design a thermal facility for combustion, gasification, or pyrolysis purposes. However, more tests should be performed considering other variables (particle diameter, gas composition along the degradation time, etc.) and conditions (temperature, air flow rate) to support the theories mentioned before.

References

1. Ambiente, A., Agência, P.: do Relatório Anual Resíduos Urbanos 2019, 2020
2. Nobre, C., Vilarinho, C., Alves, O., Mendes, B., Gonçalves, M.: Upgrading of refuse derived fuel through torrefaction and carbonization: evaluation of RDF char fuel properties. *Energy* **181**, 66–76 (2019). <https://doi.org/10.1016/j.energy.2019.05.105>
3. Ceylan, S., Topçu, Y.: Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresour. Technol.* **156**, 182–188 (2014). <https://doi.org/10.1016/j.biortech.2014.01.040>
4. Guo, Z., et al.: Study on kinetics of coal pyrolysis at different heating rates to produce hydrogen. *Fuel Process. Technol.* **107**, 23–26 (2013). <https://doi.org/10.1016/j.fuproc.2012.08.021>
5. Kumar Mohalik, N., Mandal, S., Kumar Ray, S., Mobin Khan, A., Mishra, D., Krishna Pandey, J.: TGA/DSC study to characterise and classify coal seams conforming to susceptibility towards spontaneous combustion. *Int. J. Min. Sci. Technol.* **32**, 75–88 (2022). <https://doi.org/10.1016/j.ijmst.2021.12.002>
6. Chen, Z., et al.: Characteristics and kinetic study on pyrolysis of five lignocellulosic biomass via thermogravimetric analysis. *Bioresour. Technol.* **192**, 441–450 (2015). <https://doi.org/10.1016/j.biortech.2015.05.062>
7. Kim, S.S., Ly, H.V., Kim, J., Choi, J.H., Woo, H.C.: Thermogravimetric characteristics and pyrolysis kinetics of *Alga Sagarssum* sp. biomass. *Bioresour. Technol.* **139**, 242–248 (2013). <https://doi.org/10.1016/j.biortech.2013.03.192>
8. Lu, J.J., Chen, W.H.: Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by thermogravimetric analysis. *Appl. Energy* **160**, 49–57 (2015). <https://doi.org/10.1016/j.apenergy.2015.09.026>
9. Lu, K.M., Lee, W.J., Chen, W.H., Lin, T.C.: Thermogravimetric analysis and kinetics of copyrolysis of raw/torrefied wood and coal blends. *Appl. Energy* **105**, 57–65 (2013). <https://doi.org/10.1016/j.apenergy.2012.12.050>
10. Mau, V., Gross, A.: Energy conversion and gas emissions from production and combustion of poultry-litter-derived hydrochar and biochar. *Appl. Energy* **213**, 510–519 (2018). <https://doi.org/10.1016/j.apenergy.2017.11.033>

11. Jenkins, M.B., Bexter, L.L., Miles, R. Jr., T., Miles, R.T.: Combustion properties of biomass flash. *Fuel Process. Technol.* **54**, 17–46 (1998)
12. Munir, S., Daood, S.S., Nimmo, W., Cunliffe, A.M., Gibbs, B.M.: Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. *Bioresour. Technol.* **100**, 1413–1418 (2009). <https://doi.org/10.1016/j.biortech.2008.07.065>
13. Farrokh, N.T., Suopajarvi, H., Sulasalmi, P., Fabritius, T.: A thermogravimetric analysis of lignin char combustion. *Energy Procedia* **158**, 1241–1248 (2019). <https://doi.org/10.1016/j.egypro.2019.01.413>
14. Dwivedi, K.K., Prabhansu, Karmakar, M.K., Chatterjee, P.K.: Thermal degradation, characterization and kinetic modeling of different particle size coal through TGA. *Therm. Sci. Eng. Prog.* **18**, 100523 (2020). <https://doi.org/10.1016/j.tsep.2020.100523>
15. Baraldi, P., Beltrami, C., Cassai, C., Molinari, L., Zunarelli, R.: Measurements of combustion enthalpy of solids by DSC. *Mater. Chem. Phys.* **53**, 252–255 (1998). [https://doi.org/10.1016/S0254-0584\(98\)00010-8](https://doi.org/10.1016/S0254-0584(98)00010-8)
16. Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C.: Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **86**, 1781–1788 (2007). <https://doi.org/10.1016/j.fuel.2006.12.013>



Treatment of Pig Farming Effluents by Coagulation with Alkaline Wastes, Atmospheric Carbonation, and Bioremediation with Microalgae

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Abstract. Pig farming effluents usually present high levels of suspended solids as well as organic and biological contaminants that hinder the application of conventional treatment methods. Thus, novel treatment alternatives are needed to solve the problems of point source pollution arising from pig farms. In this paper, the integrated treatment of pig farming effluents was carried out using precipitation with wastes, atmospheric carbonation, and bioremediation with microalgae. First, different alkaline wastes (biomass ash, lime sludge and grits) were evaluated as coagulation agents. The raw effluent was diluted (1:5) and pre-treated via chemical precipitation at concentrations from 25 g/L to 100 g/L. Biomass ash at the concentration of 100 g/L increased the effluent's pH to 12.56 and allowed the highest removal of total solids (64.2%) and chemical oxygen demand (87.2%). After this step, the effluent's pH was adjusted to 7 by atmospheric carbonation or the addition of concentrated H₂SO₄. The pre-treated effluent was then inoculated with microalgae cultures (*Chlorella vulgaris* and *Tetradesmus obliquus*; 10% v/v) to evaluate the removal efficiency of critical effluent parameters such as total solids, total nitrogen, total phosphorus, and chemical oxygen demand. The proposed integrated process enabled the treatment of pig farming effluents, achieving promising results for the reduction of critical parameters and promoting CO₂ capture during atmospheric carbonation and microalgae growth.

Keywords: Pig farming effluents · Integrated treatment · Atmospheric carbonation · Microalgae

1 Introduction

Pig meat is an important market worldwide with an estimated pork production of about 122 million tons in 2021 (FAO 2021). Pig rearing methods include outdoor or

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intense farming where pigs are accommodated in small houses and commonly fed with antibiotics and hormones to increase production and reduce mortality.

In China, the world’s leading pork producer, small-scale farms generate about 1300 tons of wastewater per year, including feces, urine and washing wastewater. This number equates to 4 to 8 L of wastewater per day per pig, totaling 16 kg of nitrogen (N) per animal per year (Nagarajan et al. 2019). Due to the high concentrations of pollutants present in swine effluent, such as organic matter (2000–30000 mg/L COD), total nitrogen (200–2055 mg/L) and total phosphorus (100–620 mg/L) (Cheng et al. 2019), the treatment of these effluents is still inefficient and a major challenge. As such, the integration of novel treatment processes that allow effluent remediation and recovery of valuable products are increasingly attractive. To meet these needs, this work presents an innovative and effective treatment alternative that integrates the valorization of mineral wastes as chemical precipitation agents and allows the recovery of nutrients in the form of algal biomass. Four types of alkaline wastes were evaluated as precipitants for effluent pre-treatment and atmospheric carbonation was compared with acid neutralization as a sustainable option for pH adjustment. Finally, bioremediation of the pre-treated effluent was evaluated as the main treatment process using two species of microalgae (*Chlorella vulgaris* and *Tetrademus obliquus*).

2 Material and Methods

This study was divided into three stages: (1) effluent pre-treatment through chemical precipitation, (2) neutralization and (3) remediation with microalgae, according to the figure below (Fig. 1):

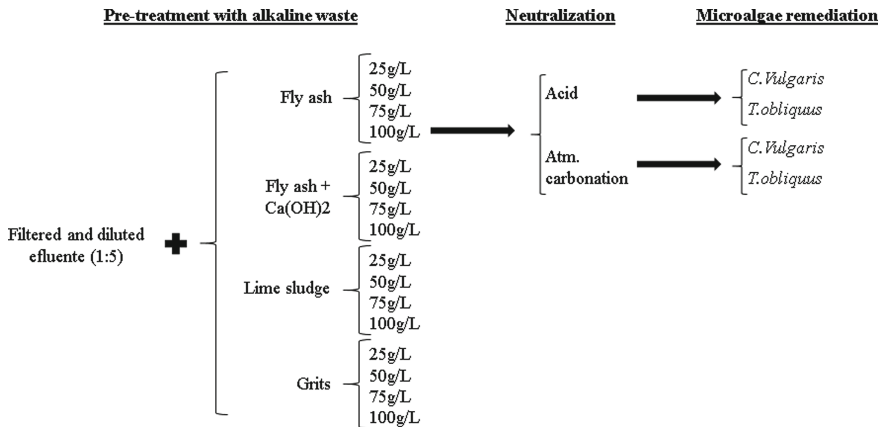


Fig. 1. Flowchart of the steps covered in the study: chemical precipitation with alkaline waste, neutralization, and bioremediation with microalgae.

Initially, the raw pig farming effluent was diluted at 1:5 with tap water and solid contaminations (sand and biomass fragments) were removed by filtration through a textile filter. The diluted effluent was then subjected to chemical treatment with alkaline

wastes (fly ash, fly ash+Ca(OH)₂, lime sludge and grits), at concentrations from 25 to 100 g/L, for 1 h, under stirring. The effluent treated with fly ash at 100 g/L was selected for further experiments and was neutralized by the addition of sulfuric acid or using forced aeration (atmospheric carbonation). Both effluents were then used as a culture medium for two species of microalgae and their potential for effluent remediation was evaluated. The following diagram presents all the steps covered in the study.

2.1 Effluent Characterization

The crude pig farming effluent was provided by Aviliz Group, an important livestock production company with farms distributed in the regions of Rio Maior, Leiria and Marinha Grande (Portugal). The effluents (25 L samples) were collected at the point of release into the first settling lagoon and presented a pasty consistency. After dilution and filtration, samples were characterized for pH (Crison MicropH 2001 m), electrical conductivity (Mettler Toledo MC226 Conductivity Meter) and chemical oxygen demand (COD) using the dichromate method (Hanna Instruments test kits). Total solids (TS) and volatile (VS) and fixed solids (FS) were determined according to standard methods (2540B and 2540E, respectively) (APHA 1985).

2.2 Precipitation with Alkaline Wastes

Four types of alkaline wastes were used as precipitants: two fly ash samples from the Mondego Thermoelectric Power Station (with and without supplementation with Ca(OH)₂) and two mineral wastes (lime sludge and grits) from The Navigator Company, a pulp and paper industry. The alkaline wastes were milled, if necessary, homogenized and sieved at 500 μm before use. The precipitation procedure was adapted from (Viegas and Gonçalves 2021). Briefly, samples of the diluted effluent (150 mL) were treated with different doses of precipitants (25 g/L, 50 g/L, 75 g/L and 100 g/L), for 1 h, under vigorous stirring. After this period, the samples were allowed to sediment for 24 h and decanted. The volume of decanted effluent was measured to determine the yield of aqueous phase. The sedimented sludge was dried in an oven at 105 °C to determine total solids (TS), subsequently ashed at 550 °C for 1 h, to determine fixed solids (FS) and volatile solids (VS) were determined by difference. The dry weight of sedimented sludge was considered as dry yield of solids relatively to the added ash mass.

Atmospheric carbonation tests were adapted from (Madeira et al. 2020) and involved forced aeration with atmospheric air. The effluent samples (1 L) pre-treated with alkaline waste, were placed in a glass cylinder of the same capacity, and atmospheric air was continuously bubbled, using an air pump connected to a diffuser stone placed in the bottom of the cylinder. This aeration regime took place at cycles of 10 h followed by 14 h of rest, at an airflow of 25 L/h.

Samples were monitored daily for pH and electrical conductivity, until a neutral pH value between 7 and 8 was reached. The effluent treated with biomass ash and after the atmospheric carbonation step were characterized for the same physicochemical parameters as described for the raw effluent.

2.3 Bioremediation with Microalgae

Two culture media were evaluated for remediation with microalgae: M1 - diluted effluent samples pre-treated with alkaline waste followed by atmospheric carbonation, and M2 - effluent treated with alkaline waste and neutralized with sulfuric acid (H_2SO_4) (Viegas, Gouveia, and Gonçalves 2021). For both media, the contents of nitrogen, phosphorus, COD, pH and electrical conductivity were analyzed before inoculation with microalgae to verify the need for dilution.

The pre-treated effluent samples (750 mL) were placed in Erlenmeyer flasks (1000 mL), sealed with hydrophobic cotton and were inoculated with 75 mL of microalgae cultures grown in BG11 medium. Two species of microalgae were used: *Chlorella vulgaris* and *Tetradismus obliquus*. Each reactor was kept continuously aerated (~ 200 mL/min), at room temperature (close to 20°C), under artificial lighting with LED fluorescent lamps, at $\pm 200 \mu\text{E m}^{-2} \text{s}^{-1}$ (digital luxmeter ROLINE, model RO 1332 A). The reactors were monitored daily for pH, electrical conductivity and optical density at 540 nm (Biochrome S4 Libra). Total nitrogen, phosphorus and COD were determined weekly (Hanna Instruments kits) to evaluate the bioremediation efficiency. Phosphorus was supplemented weekly to reach a concentration of 10 mg P/L, to compensate the low concentration in the pre-treated effluents. Microalgae growth was also analyzed weekly by determining the dry weight of a 10 mL sample filtered on a glass microfiber filter (MFV3047-FILTER-LAB).

Analytical results were determined in duplicated and presented as average values and standard deviations.

3 Results and Discussion

3.1 Precipitation with Alkaline Wastes

Since the pig farming effluent is composed of urine, feces and washing water from pig breeding sites, raw samples had a sludge consistency and were rich in solids and residues. Their general characteristics were also due to the sampling point being in the entry point of the reception lagoon before settling and decantation can occur. The dilution of the raw effluent allowed a reduction of total solids and facilitated filtration of the diluted effluent using textile filters to separate some mineral wastes and biomass fragments.

The alkaline wastes used in the precipitation experiments were fly ash from a biomass thermal power plant and mineral wastes from pulp and paper production. These wastes are generated in large amounts and often landfilled, a non-sustainable option with the generation of no added value. The four wastes were evaluated as precipitants at doses from 25 g/L to 100 g/L and the yields of decanted effluent and precipitated solids are presented in Table 1.

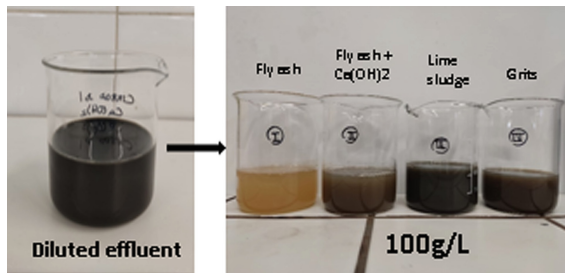
The yield of decanted effluent varied from 63.43% to 87.98% (v/v) since some components of the diluted effluent precipitated and a fraction of the liquid is retained in the sedimented sludge. On the other hand, the yield of precipitated solids was always higher than 100%, which means that the solids precipitated during the treatment corresponded to a higher mass fraction than the mineral waste components dissolved in the effluent.

Table 1. Yields of the chemical precipitation process using different alkaline wastes at different doses and physic-chemical properties of the liquid phases recovered.

Precipitant	Dose (g/L)	Aq. Yield (%)	Sol. Yield (%)	pH	E.C. (mS/cm)
Fly ash	25	87.98	138.45	10.02	3.41
	50	76.61	130.30	11.83	4.28
	75	65.19	124.00	12.59	8.95
	100	63.43	119.06	12.56	9.43
Fly ash+Ca(OH) ₂	25	81.35	176.29	9.31	3.66
	50	79.60	138.76	8.95	4.12
	75	76.25	127.80	11.75	3.33
	100	69.08	118.86	11.83	3.77
Lime sludge	25	84.27	140.92	8.42	4.11
	50	81.14	121.71	8.68	3.96
	75	79.53	109.88	8.90	3.89
	100	78.14	104.14	8.67	3.82
Grits	25	83.23	167.60	9.45	4.16
	50	81.23	134.77	10.30	4.04
	75	72.54	122.34	11.04	4.47
	100	68.21	117.88	11.15	5.15

For all tested wastes, increasing the dose of alkaline waste led to an increase in the effluent's pH, thus signaling an increased dissolution of alkaline species. Moreover, effluent conductivity was only positively correlated with the alkaline waste dose for both fly ash and grits. This behavior reflects a higher dissolution of waste components in the liquid phase which affects the chemical equilibrium of the treated effluent.

The effect of the multiple chemical reactions in the turbidity of the liquid phase is illustrated in Fig. 2.

**Fig. 2.** Result of pretreatment with 100 g/L for each of the four precipitants.

From Fig. 2, it can be observed that the solutions that reached a higher pH also showed a higher clarification, an indication that deprotonation of organic species is involved in the process of complexation and precipitation. This change in pH can also affect the dissolution of inorganic salts therefore affecting the mineral composition of the treated effluent.

Total, Volatile and Fixed Solids

Regarding the removal of solids present in the decanted aqueous phase, the following concentrations were obtained for TS, VS and FS, as shown in Table 2.

Table 2. Removal of solids after pretreatment.

	TS (g/L)	VS (g/L)	FS (g/L)	
Raw Effluent (1:5)	18.84	8.74	10.1	
Precipitant	Dose			
Fly ash	25 g/L	6.40	3.08	3.32
	50 g/L	5.54	1.82	3.72
	75 g/L	6.02	0.46	5.56
	100 g/L	6.96	0.44	6.52
Fly ash+Ca(OH) ₂	25 g/L	5.74	3.04	2.70
	50 g/L	5.82	2.82	3.00
	75 g/L	4.94	2.02	2.92
	100 g/L	4.90	1.40	3.50
Lime sludge	25 g/L	5.10	2.84	2.26
	50 g/L	4.82	2.50	2.32
	75 g/L	4.92	2.40	2.52
	100 g/L	5.22	2.78	2.44
Grits	25 g/L	6.28	3.22	3.06
	50 g/L	7.48	3.50	3.98
	75 g/L	6.94	2.70	4.24
	100 g/L	7.64	3.04	4.60

The chemical pre-treatment with alkaline wastes caused large reductions in TS (around 70%), but also VS and FS, confirming the elimination of organic and inorganic contaminants in the treated effluents for all tested wastes.

Fixed solids increased with the dose of alkaline waste especially for fly ash and grits. These results reflect the dissolution of the alkaline wastes in the effluent, and are coherent with the previously presented results of pH and conductivity.

On the other hand, VS decreased for all alkaline wastes but a positive correlation with the applied dose was only observed for fly ash and fly ash+Ca(OH)₂. The effluent treated with fly ash presented the highest removal of VS but the lowest removal of FS. The results indicate that coagulation and precipitation of organic species strongly contribute to the effluent's clarification.

Chemical Oxygen Demand (COD)

After pre-treatment with alkaline wastes, at the different doses, COD was determined for all treated effluents to evaluate the presence of oxidizable species that would require removal in subsequent treatment steps (Table 3).

Table 3. COD values for the raw effluent and after pre-treatment with alkaline wastes.

COD (mg O ₂ /L)				
Raw Effl.	71000			
Dose	Fly ash	Fly ash+Ca(OH) ₂	Lime sludge	Grits
25 g/L	40500	42500	38000	41100
50 g/L	26800	40400	35000	42100
75 g/L	11400	29500	34600	36400
100 g/L	9100	20800	36800	40000

All alkaline wastes were able to reduce COD which was to be expected given their capacity to reduce TS. Fly ash presented the best results, reaching a removal of 87% of COD at a dose of 100 g/L. Globally, the alkaline wastes that allowed a higher reduction of the solution pH (fly ash and fly ash+Ca(OH)₂) also had the highest efficiency in the removal of VS, COD and turbidity.

3.2 Neutralization

Given the better efficiency in reducing VS and COD, the pre-treatment with fly ash at a 100 g/L dose was selected for further experiments. Considering that the pre-treated effluent had a pH of 12.56, neutralization of the medium was required before inoculation with microalgae. This neutralization step was performed by pH adjustment with concentrated sulfuric acid (H₂SO₄), or by atmospheric carbonation (forced aeration), a method that enables a decrease of pH by CO₂ dissolution in the aqueous medium and avoids mineral acid consumption.

Atmospheric carbonation tests occurred for 32 days, but the pH and electrical conductivity (EC) values, that were monitored daily, stabilized after 15 days, at the final values of 8.85 and 6.78 mS/cm, respectively. For the effluent neutralized with acid COD values were of 8470 and 9380 mg O₂/L, values similar to the COD value (9100 mg O₂/L) of the effluent before neutralization. This may be due to the dissolution of sulfate ions in the effluent that compensates some precipitation of dissolved or suspended solids. When neutralization was performed by atmospheric carbonation, the dissolution of carbonate

ions in the effluent did not have an equivalent contribution and a significant reduction of COD (47%) was observed relatively to the value obtained after treatment with fly ash.

3.3 Bioremediation with Microalgae

Bioremediation of the pre-treated effluent, neutralized with acid or by atmospheric carbonation, was evaluated for 21 days, in batch mode, using the microalgae *C.vulgaris* and *T.obliquus*. Cell concentration and microalgae growth rate, as well as initial and final values of the effluent critical parameters are presented in Table 4.

Table 4. Microalgae growth and nutrient removal efficiency for bioremediation tests of effluent neutralized with acid or by atmospheric carbonation, with *C.vulgaris* and *T.obliquus* microalgae.

<i>C.vulgaris</i>				
Parameter (mg/L)	Neut. With Acid (M1)		Carbonation (M2)	
	Initial	Final	Initial	Final
COD	8470	4680	4810	1731
Total N	330	270	20	170
Total P	8.4	0	1.8	0
Cell conc. (mg/L)	1260	1660	540	920
Growth rate (mg/L.d)	19.1		18.1	
<i>T.obliquus</i>				
Parameter (mg/L)	Neut. With Acid (M1)		Carbonation (M2)	
	Initial	Final	Initial	Final
COD	9380	4390	4810	2192
Total N	320	280	20	80
Total P	3.8	0	1.8	0
Cell conc. (mg/L)	1060	1080	880	1520
Growth rate (mg/L.d)	1.0		30.5	

Both effluents, presented COD values higher than 4800 mg O₂/L, but very low concentrations of phosphorus (1.8 to 8.4 mg/L), values that may limit microalgae growth, given the role of phosphorus in ATP synthesis to support the energy-required processes in microalgae metabolism (Su, Y. 2021). Nitrogen concentration for the effluent neutralized with acid was in the range of 270 to 330 mg/L, but in the case of the effluent neutralized

by atmospheric carbonation, was of 20 mg/L, a value that could also limit algal biomass production and therefore the bioremediation process (Yaakob, Mohamed, Al-Gheethi, Gokare, and Ambati 2021).

Despite of the challenging composition of the pre-treated effluents, both microalgae were able to grow and reduce COD (44.7% to 53.2% for M1 and 54.4% to 64.0% for M2), therefore performing some bioremediation of the effluents.

Initial microalgae cell concentrations varied from 540 to 1260 mg/L and had a moderate to vestigial growth, probably motivated by the low concentrations of N and P species in the pre-treated effluents. Total P value was reduced to zero after microalgae growth, confirming the full consumption of the initial concentrations present in the effluent as well as the 10 mg P/L weekly supplementation. Nitrogen concentration was slightly reduced for the effluents neutralized with mineral acid (12.5% for *T. obliquus* and 18.2% for *C. vulgaris*), a behavior that reflects some metabolic limitations since nitrogen initial concentrations were above 300 mg/L in these effluents and microalgae generally show a high ability to remediate nitrogen species (Chen and Wang 2020).

For the effluent M2, neutralized by atmospheric carbonation, initial nitrogen concentration was of 20 mg/L, the microalgae inoculum accounted for around 24 mg/L additional N from the BG11 medium, but final concentrations were higher (80 and 170 mg/L). These results may reflect the death of a fraction of the microalgae cells from the inoculum, releasing the cell nutrients into the aqueous medium. New cells formed during the bioremediation test were not able efficiently remove nitrogen from the solution resulting in a slight increase in total N.

All cultures were regularly observed under a microscope, and it was concluded that despite the pH of 12 achieved during the pre-treatment some bacteria and protozoa species still resisted and could be observed in the effluent during the experiments. These microorganisms can have a synergistic effect on microalgae bioremediation by consuming O₂ and nutrients from the effluents and producing CO₂ during this metabolic process (Bhatia et al. 2022).

4 Conclusions

The chemical precipitation of suspended and dissolved materials from raw pig farming samples using alkaline wastes as coagulating agents is a sustainable and efficient approach for the pre-treatment of these effluents. The alkaline waste composition and dose strongly influence the efficiency of the precipitation process and the final characteristics of the pre-treated effluent. Removal efficiencies of 63% for TS, 95% for VS, and 87% for COD were achieved with fly ash treatment at a 100 g/L dose. The neutralization of the pre-treated effluent by atmospheric carbonation allowed to reach a pH of 7–8, compatible with microalgae growth, but lowered total N and total P concentrations to very low values, conditions that led to a poor microalgae growth. Both microalgae were able to reduce COD of the effluents, even under limited cell growth. Dilution of the pre-treated effluent with raw effluent to achieve adequate phosphorus and nitrogen concentrations may be adopted to compensate these effects. In general, this study showed promising results for the integrated treatment of pig farming effluents using chemical precipitation with biomass ash, neutralization by atmospheric carbonation and bioremediation

with microalgae. This strategy is also an economic and sustainable solution to recover nutrients from pig farming effluents and promote CO₂ capture.

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References

- APHA: Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington DC (1985)
- Bhatia, S., et al.: An overview on microalgal-bacterial granular consortia for resource recovery and wastewater treatment. *Biores. Technol.* **351**, 127028 (2022). <https://doi.org/10.1016/j.biortech.2022.127028>
- Chen, H., Wang, Q.: Microalgae-based nitrogen bioremediation. *Algal Res.* **46**, 101775 (2020). <https://doi.org/10.1016/j.algal.2019.101775>
- Cheng, D.L., et al.: Microalgae biomass from swine wastewater and its conversion to bioenergy. *Biores. Technol.* **275**, 109–122 (2019). <https://doi.org/10.1016/j.biortech.2018.12.019>
- FAO: Meat Market Review (2021). <https://www.fao.org/3/cb7886en/cb7886en.pdf>
- Madeira, L., Almeida, A., Teixeira, M., Prazeres, A., Chaves, H., Carvalho, F.: Immediate one-step lime precipitation and atmospheric carbonation as pre-treatment for low biodegradable and high nitrogen wastewaters: a case study of explosives industry. *J. Environ. Chem. Eng.* **8**(3), 103808 (2020). <https://doi.org/10.1016/j.jece.2020.103808>
- Nagarajan, D., Kusmayadi, A., Yen, H., Dong, C., Lee, D.: Current advances in biological swine wastewater treatment using microalgae-based processes. *Biores. Technol.* **289**, 121718 (2019). <https://doi.org/10.1016/j.biortech.2019.121718>
- Silveira, C.F., De Assis, L.R., Paulo, A., Oliveira, D.S., Calijuri, M.L.: Valorization of swine wastewater in a circular economy approach: effects of hydraulic retention time on microalgae cultivation. *Sci. Total Environ.* **789**, 147861 (2021). <https://doi.org/10.1016/j.scitotenv.2021.147861>
- Su, Y.: Revisiting carbon, nitrogen, and phosphorus metabolisms in microalgae for wastewater treatment. *Sci. Total Environ.* **762**, 144590 (2021). <https://doi.org/10.1016/j.scitotenv.2020.144590>
- Viegas, C., Gonçalves, M.: Integrated treatment of pig production wastewaters using pre-treatment with biomass ash and bioremediation by microalgae. *Acta Scientific Agriculture* **5**(7), 44–57 (2021)
- Viegas, C., Gouveia, L., Gonçalves, M.: Bioremediation of cattle manure using microalgae after pre-treatment with biomass ash. *Bioresource Technology Reports* **14**, 100681 (2021). <https://doi.org/10.1016/j.biteb.2021.100681>
- Yaakob, M.A., Mohamed, R., Al-Gheethi, A., Ravishankar, G.A.: Influence of nitrogen and phosphorus on microalgal growth, biomass, lipid, and fatty acid production: an overview. *Cells* **10**, 393 (2021). <https://doi.org/10.3390/cells10020393>



Dry and Hydrothermal Carbonization of Mixtures of Refuse Derived Fuels, Waste Biomass, and Sewage Sludge

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Abstract. In this work, the carbonization process was applied as a pretreatment to valorize mixed wastes by producing chars with better fuel properties and more suitable to be used as feed in gasification processes. For this purpose, different types of wastes (Refused Derived Fuel, dry sewage sludge, and pinewood waste) and their blends (RDF/sludge, RDF/biomass, and RDF/sludge/biomass) were carbonized at temperatures between 250 and 420 °C. Dry carbonization (DC) and hydrothermal carbonization (HTC) were performed in a range of temperatures between 360–420 °C and 250–300 °C, respectively. The samples were composed of different ratios of each waste to evaluate possible synergies in the carbonization process. The biochar yield varied between 78.3 to 37.7% and the hydrochar yield was between 60.7 and 52.7%. Proximate and elemental composition, chlorine content, mass, and energy yields were determined for the original samples and the chars produced to access the fuel properties improvement and evaluate the most efficient condition of mixed waste carbonization. Dry and wet carbonization lead to an increase in carbon content and heating value but only hydrothermal carbonization yielded chars with lower chlorine content than the original materials. Biomass and sludge incorporation did not have an advantageous effect on the properties of the obtained chars.

Keywords: Dry carbonization · Hydrothermal carbonization · Mixed wastes

1 Introduction

Energetic valorization of wastes that are not viable to be recycled is an effective way to increase the value of the waste management process and divert an enormous amount of high energetic materials from landfills. In this context, the production of refused-derived

fuel (RDF) by mechanical-biological treatment plants appears as an important approach to increasing resource efficiency by reintroducing this waste fraction into the production chain as an alternative fuel. However, the utilization of RDF as a substitute for fossil fuels faces several constraints related to the high heterogeneity, high moisture content, high chlorine content, and low density of the raw waste.

To overcome the issues abovementioned, the thermochemical processes of dry and wet carbonization may have an important contribution to producing biochars and hydrochars more homogeneous and with lower moisture and chlorine content, higher heating values, and upgraded physical characteristics that may improve their combustible properties and reduce associated costs of storage and transportation. The dry carbonization of RDF and other waste streams to obtain biochars with improved fuel properties is described by many authors. Nobre et al. [1] produced biochars with a high calorific value (20.1–26.2 MJ/kg) after dry carbonization (300–400 °C) of low-chlorine RDF. In a higher range of temperature, Haykiri-Acma et al. [2] concluded that to produce biochar with upgraded fuel properties the temperature of carbonization must not exceed 400 °C. Carbonization of plastic-containing wastes was also described as an important step as pretreatment before the gasification process. Recari et al. [3] applied carbonization at 320 °C in solid recovered fuel (SRF) samples before gasification and reported some advantages of using this pretreatment mainly related to lower contaminant emissions during gasification tests. In the same way, Alves et al. [4] reported some benefits such as increasing the calorific value of syngas, reduced emission of HCl and tars, and increased apparent density of the RDF chars.

DC and HTC of different types of biomass are commonly described to improve the physical and fuel properties of chars when compared with the raw material, and some works have also gained attention by applying this pretreatment in other waste streams, such as sewage sludge (SS) [5]. Chen et al. [6] also reported the HTC of SS as an efficient process to recover useful products and mitigate environmental pollution risks, highlighting the phosphorous recovery on the hydrochars. Some studies have emphasized the synergetic effect of co-HTC of plastics and biomass regarding combustible properties upgrade and high dechlorination efficiency of the solid fraction. As an example Shen et al. [7] reported the co-HTC of plastic with biomass produced a more homogeneous hydrochar with higher heating value, lower granulometry, and reduced plastic agglomerates. Huang et al. [8] also mentioned that at the same time the synergetic effect of co-HTC removes Cl from PVC it takes out the alkalis from biomass and produces hydrochars with improved high heating value (HHV).

In this work, dry and wet carbonization (HTC) were proposed as a pretreatment aiming the production of biochars and hydrochars with increased fuel properties and reduced chlorine content to be applied directly in the combustions process or submitted to more efficient thermochemical processes such as gasification.

2 Materials and Methods

2.1 Raw Materials

Three different types of wastes namely RDF, dry sewage sludge (SS), and pinewood biomass (PB) were submitted to the dry and wet carbonization processes. The samples

were carbonized alone or in blends with different proportions to assess the synergetic effect of the mixtures. Initially, the RDF sample was manually cut to obtain a smaller granulometry (less than 10 mm). The RDF used in this work was produced from municipal solid wastes treated in a mechanical-biological treatment facility and provided by Braval S.A. It is composed of a mixture of plastic, paper, textiles, wood, and miscellaneous and presents an initial moisture content of 5.9%. The dry sewage sludge was obtained from a municipal wastewater treatment plant. Before the carbonization tests, this waste was crushed and sieved to a 2 mm size and had an initial moisture content of 10%. The pinewood biomass was received in the sawdust form with a moisture content of 9.4%. Figure 1 shows the aspect of the wastes before being submitted to the carbonization tests.

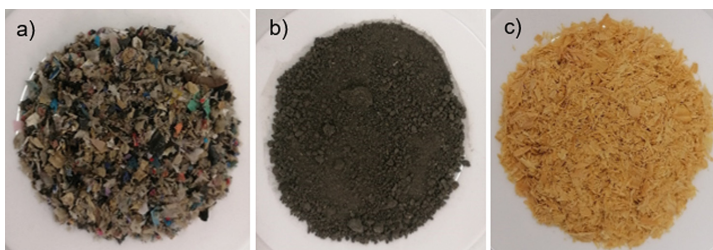


Fig. 1. The raw wastes used in the carbonization experiments: a) RDF; b) Dry sewage sludge; and c) Sawdust pinewood biomass.

2.2 Dry Carbonization Tests

The dry carbonization experiments occurred in a muffle furnace (Nabertherm® L3/1106). The temperature of carbonization varied between 360 and 420 °C and the residence time was 30 min for all the experiments. In each run, five porcelain crucibles were filled with the samples and placed inside the muffle furnace. In total, 16 carbonization tests were performed at varying the temperature and the sample mixture composition. The samples composed of unblended RDF and sewage sludge as well as the sample composed of a blend of 75% RDF and 25% pinewood biomass were carbonized at four different temperatures (360, 380, 400, and 420 °C) to assess the effect of increase carbonization severity on the characteristics of the biochar. To assess the effect of the sample's composition on the characteristics of the biochar, four different blends composed of 75% RDF and 25% SS, 50% RDF and 50% SS, 56.3% RDF, 18.8% PB, and 25% SS and 37.5% RDF, 12.5% PB, and 50% SS were carbonized at 400 °C for 30 min.

2.3 Hydrothermal Carbonization Tests

The HTC experiments were carried out using a 1L stirred batch reactor (Parr Pressure Reactor) coupled with an electric heater and controller (Parr 4848 Reactor controller),

under autogenous pressure. For each test, the reactor was loaded with the solid sample and distilled water in a mass ratio of 1:4. The temperatures of 250 and 300 °C were chosen in a residence time of 30 min. The samples composed of unblended RDF, SS, and the blend of 75% RDF and 25% PB were submitted to HTC at both temperatures. To assess the effect of sample composition, the same four different blends used in DC tests were submitted to HTC at 300 °C for 30 min. In total, 10 HTC experiments were carried out. After each test, the solid phase (hydrochar) was separated by the liquid fraction by filtration and dried overnight at 105 °C. The liquid phase was stored at 4 °C for further analysis. The hydrochars were then exposed to air for 5 days to equilibrate the moisture content.

2.4 Characterization of Raw Wastes, Biochars, and Hydrochars

The raw wastes, biochars, and hydrochars were characterized according to proximate and ultimate composition, mass and energy yield, low calorific value, and chlorine content. Moisture, volatile matter, and ash contents were determined according to CEN/TS 15414-3:2010, EN 15402:2011, and EN 15403:2011, respectively, while Fixed carbon content was obtained by difference, on a dry basis. Ultimate analysis (carbon, hydrogen, nitrogen, and sulfur) was performed using an elemental analyzer (Thermo Finnigan – CE Instruments Model Flash EA 112 CHNS series). Oxygen content was calculated by difference on a dry ash-free basis. Low heating values (LHV) of the raw wastes and the char samples were determined by estimation according to Hosokai 2016[9], expressed in Eq. (1).

$$LHV(kJ/g) = 38.2mC + 84.9(mH - mO/8) - \Delta H_l \quad (1)$$

where mC, mH, and mO are the contents of carbon, hydrogen, and oxygen, respectively; ΔH_l described latent heat.

The mass and energy yields of the produced chars (on a dry basis) were calculated based on Eqs. (2) and (3), respectively:

$$Mass\ yield(\%) = \frac{m_{char}}{m_{raw}} \times 100 \quad (2)$$

$$Energy\ Yield(\%) = Mass\ yield \times \frac{LHV_{char}}{LHV_{raw}} \quad (3)$$

where m_{char} and LHV_{char} are the mass (kg) and low heating value of the chars (MJ/kg); m_{raw} and LHV_{raw} are the mass and low heating value of the raw wastes. Chlorine content was determined through X-Ray fluorescence (Niton XL 3T Gold ++). Dechlorination efficiency (DE) was calculated according to Zhang et al.[10] and expressed in Eqs. (4):

$$DE(\%) = \left(1 - \frac{Cl\ content\ in\ char \times n_{yield}}{Cl\ content\ in\ raw}\right) \times 100 \quad (4)$$

where n yield is the mass yield of the chars.

3 Results and Discussion

The moisture content of the raw wastes and the chars produced at different carbonization conditions were determined after the samples were air-exposed to equilibrate with atmospheric humidity. The SS had the higher initial moisture content among the raw wastes with values being around 10%, followed by PB and RDF samples with 9.5 and 5.9%, respectively. Increasing carbonization temperature led to an increase in the hydrophobicity of the chars and, consequently, the moisture reduction in all the samples compared with the raw wastes. The volatile matter decreased with carbonization severity conditions except for the unblended RDF chars samples produced by dry carbonization as shown in Table 1. Also, the volatile matter was higher for hydrochars when compared with the biochar produced for the same waste composition. The higher values were found for the RDF hydrochars (77–79%).

Regarding the ash content, as expected, the increasing carbonization temperatures are directly related to the increase of ash on the produced chars. For RDF-containing samples, the biochars had a higher ash concentration when compared to the hydrochars while the opposite trend was observed for the SS samples. For those, the highest ash value was 52% at the higher HTC temperature test. Even though the fixed carbon increment was observed after both carbonization processes, it was more evident in the biochars than in hydrochars. For SS hydrochars the values of fixed carbon were even lower on the hydrochars when compared with the raw waste. The highest fixed carbon concentration was found in the 75% RDF + 25% biomass biochars samples reaching values of 21.9 to 26.7%.

Ultimate analysis showed that carbon content increased in the chars after the carbonization processes. It was more pronounced in dry carbonization with higher temperature for RDF samples (420 °C) and at 400 °C for the RDF with the incorporation of biomass. This value had insignificant changes on chars produced by SS samples. The hydrogen content also increased while oxygen has decreased with more carbonization severity, probably due to the dehydration and decarboxylation processes at this range of temperature [11].

Chlorine content in the biochars produced at lower temperatures (360°) was higher than the raw waste in the RDF-containing samples. Increasing carbonization temperatures led to a decrease in the chlorine on the biochars produced being around 1.5 and 1.1% on the RDF and RDF with biomass incorporation samples at 420 °C. For SS samples, the carbonization does not seem to affect the chlorine content on the biochar. However, the highest reduction in chlorine content was observed for the HTC experiments. For the RDF sample, the HTC at 300 °C seems to be effective in the chlorine reduction reaching the lowest value for all the tests (0.75%). Even though a chlorine reduction was observed as biomass is incorporated into the RDF sample, the decrease in this parameter was lower than in the unblended samples. In the HTC experiments, chlorine reduction also was observed for the SS hydrochar sample. In this way, the addition of small amounts of SS may boost the chlorine reduction in the RDF sample as observed in Table 1.

Table 1. Sample composition, proximate analysis, ultimate analysis, and chlorine content of the raw wastes and chars produced by DC and HTC.

Sample	T (°C)	Sample composition (%)			Proximate analysis (wt%. db)				Ultimate analysis (wt%. db)					Cl ^b
		RDF	SS	PB	M	VM	FC	Ash	C	H	N	S	O ^a	
Raw RDF	–	100	–	–	5.9	85.0	5.0	10.4	45.8	5.9	1.0	0.1	36.9	2,68
Raw SS	–	–	100		10.0	58.6	4.1	37.3	33.1	4.5	3.5	1.3	20.3	0.72
Raw PB	–	–	–	100	9.5	84.9	14.7	0.4	50.4	6.4	0.1	0	43.0	0.14
DC-1	360	100	–	–	2.7	61.3	21.7	15.2	58.4	3.8	1.7	0	21.0	3.31
DC-4	380	100	–	–	2.0	63.7	20.8	15.6	60.8	5.0	1.5	0.2	17.1	2.59
DC-7	400	100	–	–	3.0	65.1	17.7	17.2	59.9	5.3	1.5	0.2	16.0	1.89
DC-14	420	100	–	–	1.5	63.5	18.6	17.9	66.6	6.6	1.5	0.1	7.3	1.48
DC-2	360	–	100	–	4.4	51.6	7.7	40.7	34.5	3.8	3.5	1.4	16.0	0.64
DC-5	380	–	100	–	4.0	51.1	7.2	41.7	34.3	4.0	3.6	1.3	15.2	0.61
DC-8	400	–	100		3.0	44.6	8.3	47.1	32.6	2.7	3.4	0	14.4	0.65
DC-15	420	–	100	–	2.8	44.5	7.7	47.8	33.4	3.2	3.5	1.2	10.9	0.70
DC-3	360	75	–	25	2.7	62.7	24.1	13.2	62.3	4.9	1.4	0.1	18.1	3.38
DC-6	380	75	–	25	2.1	62.0	21.9	16.1	61.1	4.5	1.4	0.2	16.8	0.90
DC-9	400	75	–	25	2.8	58.2	24.6	17.2	64.5	5.4	1.3	0	11.6	1.50
DC-16	420	75	–	25	1.6	49.7	26.7	23.6	61.9	5.3	1.2	0.2	7.7	1.12
DC-10	400	75	25	–	2.2	56.2	17.5	26.2	59.2	5.4	2.0	0.2	7.0	2.29
DC-11	400	50	50	–	3.6	53.4	13.7	32.9	50.1	4.6	2.5	0.5	9.3	1.47
DC-12	400	56.3	25	18.7	4.1	53.7	23.2	23.2	59.1	5.0	1.8	0.3	10.6	1.05
DC-13	400	37.5	50	12.5	3.8	53.5	14.0	32.5	57.7	4.8	2.3	0.3	2.4	1.14
HTC-1	250	100	–	–	3.6	79.0	8.2	12.9	51.1	4.9	1.7	0.1	29.4	1.11
HTC-4	300	100	–	–	2.6	77.3	8.3	14.5	34.6	3.8	2.2	1.4	9.2	0.75
HTC-2	250	–	100	–	5.6	47.6	3.6	48.9	60.1	5.6	1.8	0.2	22.7	0.44
HTC-5	300	–	100	–	2.7	44.7	3.3	52.0	57.6	5.1	2.2	0.0	20.6	0.33
HTC-3	250	75	–	25	7.0	71.3	19.0	9.7	33.3	3.4	1.7	0.0	9.6	1.15
HTC-6	300	75	–	25	3.1	73.6	15.9	10.5	61.6	5.0	1.8	0.0	21.0	1.39
HTC-7	300	75	25	–	1.9	70.0	7.1	22.9	46.0	4.1	2.3	0.0	24.7	0.45
HTC-8	300	50	50	–	2.5	67.0	1.0	32.1	39.0	3.7	1.9	0.0	23.4	0.42
HTC-9	300	56.3	25	18.7	3.0	66.3	12.9	20.9	51.5	4.5	2.0	0.2	20.9	0.37
HTC-10	300	37.5	50	12.5	2.5	59.5	9.5	31.0	44.4	4.3	2.0	0.4	17.9	0.34

a – By difference;

b – wt%, db.

As expected, the mass yield of the chars decreased with the increase in the carbonization temperature (Table 2). However, in all carbonization tests, the mass yield was higher than 50% except for the DC of RDF with incorporated biomass at 420 °C (37.7%). It may occur due to the high degradation of biomass constituents at this range of temperature [12]. Carbonization also led to an increase in fuel ratio and a decrease in the H/C and O/C ratio that may be reflected in the LHV of the chars. Increased LHV was observed for the biochars produced at a higher temperature (420 °C) for the RDF samples (29.7MJ/kg) and a slightly milder temperature (400 °C) for the RDF with biomass incorporated sample (27.3MJ/kg) (Fig. 2a). The incorporation of biomass and SS to the RDF samples also showed high values of LHV (around 25MJ/kg) (Fig. 3a) and may appear as an attractive way to increase the calorific value at the same time that reduces the chlorine content of the biochars.

Energy yield reached a maximum value for the biochar produced from unblended RDF at 420 °C (88%). On the other hand, increasing carbonization temperature had a negative effect on the energy yield of the biochars produced from the RDF and biomass mixture. In these samples, the highest energy yield was observed at the lower carbonization temperature (81.5%).

Regarding dechlorination efficiency, the highest temperature of dry carbonization seemed to be more effective in the RDF-containing samples (70.4 and 79.3%). In this case, the addition of biomass has shown a synergetic effect on the dechlorination process (Fig. 2b). Moreover, the HTC was demonstrated to be more efficient to reduce chlorine content on the chars than dry carbonization[10]. At 300 °C the DE of the RDF sample was 84.7%. However, the highest values of DE were observed in the samples composed of RDF with SS incorporation and the samples composed of a mixture of RDF, SS, and biomass. Compared to the DC, the HTC of the mixture samples seemed to have a high synergetic effect to increase the dechlorination efficiency (Fig. 3b).

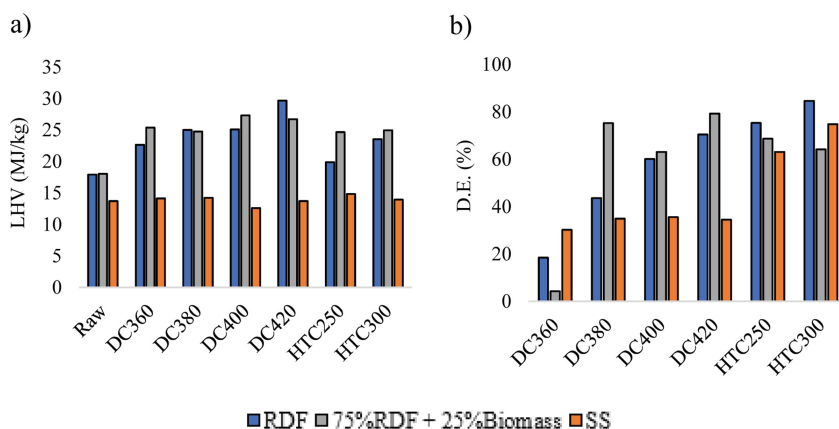


Fig. 2. (a) Low heating value and (b) dechlorination efficiency of the chars produced by DC and HTC of RDF, SS, and the mixture of RDF and biomass.

Table 2. Mass yield, fuel characteristics, and dechlorination efficiency after DC and HTC processes.

Sample	Mass yield (%)	Fuel ratio	Atomic ratio		LHV (MJ/kg)	Energy yield (%)	D.E. (%)
			FC/VM	H/C			
Raw RDF	–	0.06	1.53	0.60	17.9	–	–
Raw SS	–	0.07	1.63	0.46	13.7	–	–
Raw PB	–	0.17	1.53	0.64	18.4	–	–
DC-1	66.0	0.35	0.78	0.27	22.6	83.3	18.5
DC-4	58.3	0.33	0.98	0.21	25.0	81.4	43.6
DC-7	56.7	0.27	1.07	0.20	25.1	79.5	60.1
DC-14	53.4	0.29	1.19	0.08	29.7	88.6	70.4
DC-2	78.3	0.15	1.34	0.35	14.1	80.6	30.2
DC-5	76.1	0.14	1.39	0.33	14.2	78.9	34.9
DC-8	70.6	0.19	0.98	0.33	12.6	64.9	35.6
DC-15	67.2	0.17	1.14	0.24	13.7	67.2	34.5
DC-3	57.9	0.39	0.94	0.22	25.4	81.6	4.3
DC-6	55.9	0.35	0.89	0.21	24.8	76.9	75.3
DC-9	50.2	0.42	1.00	0.14	27.3	76.0	63.1
DC-16	37.7	0.54	1.03	0.09	26.7	55.8	79.3
DC-10	58.5	0.31	1.10	0.09	25.9	89.6	39.0
DC-11	53.9	0.26	1.11	0.14	21.5	73.3	53.2
DC-12	53.1	0.43	1.02	0.13	25.1	78.6	67.6
DC-13	57.6	0.26	1.00	0.03	25.3	91.9	52.3
HTC-1	59.5	0.10	1.14	0.43	19.9	66.1	75.4
HTC-4	55.0	0.11	1.06	0.27	23.5	72.2	84.7
HTC-2	60.7	0.07	1.32	0.20	14.8	65.6	63.1
HTC-5	55.1	0.07	1.21	0.22	13.9	55.9	74.8
HTC-3	55.7	0.27	1.11	0.28	24.7	76.3	68.7
HTC-6	52.9	0.22	0.98	0.26	25.0	73.4	64.2
HTC-7	55.9	0.10	1.08	0.40	17.8	59.1	88.4
HTC-8	57.7	0.01	1.12	0.45	14.9	54.4	85.6
HTC-9	52.7	0.19	1.04	0.30	20.6	64.0	88.6
HTC-10	54.2	0.16	1.16	0.30	18.1	61.8	86.7

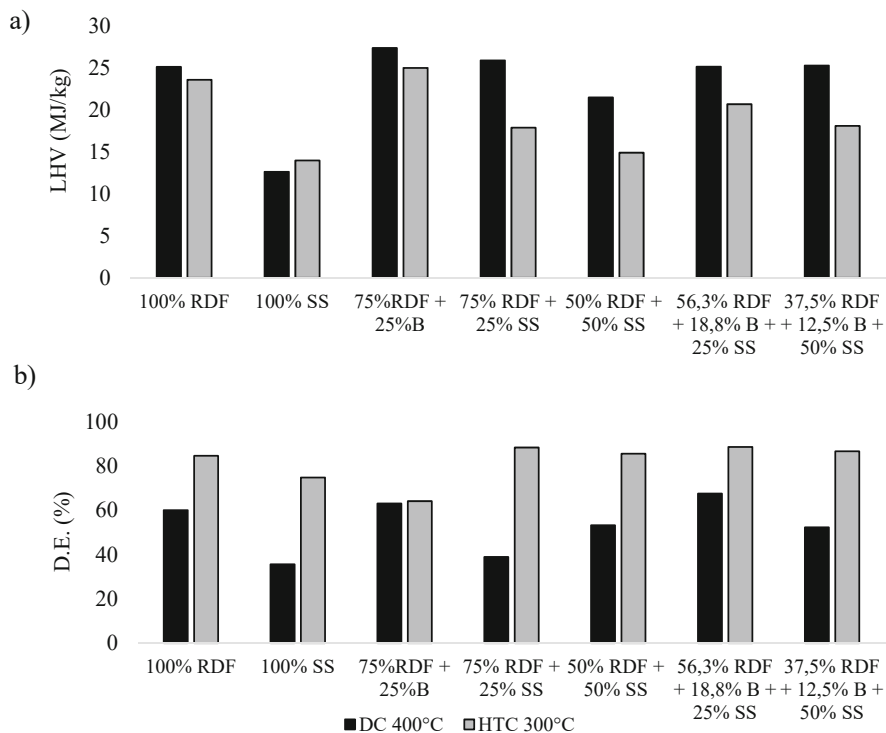


Fig. 3. (a) Low heating value and (b) dechlorination efficiency after DC at 400 °C and HTC at 300 °C experiments of different sample composition.

4 Conclusion

Dry carbonization and hydrothermal carbonization of RDF, SS, and PB and their mixtures in different proportions seem to be an effective pretreatment to produce chars with improved calorific value and diminished chlorine content. Nevertheless, high temperatures of carbonization are required in the samples composed of unblended RDF when compared with the sample with biomass incorporation. Dry carbonization had more effect in the improvement of LHV of the chars while HTC was more effective regarding the dechlorination process. Taking into the account the calorific value increment and the chlorine content below 1% required to be used as a fuel, the HTC at 300 °C of unblended RDF and the mixture of 56.3% RDF, 18.7% PB, and 25% SS appear as interesting conditions to produce chars with increased LHV and low chlorine content to be applied as a fuel. Even though dry carbonization has produced biochars with good fuel properties, the incorporation of biomass must be further studied to find the best ratio to reduce chlorine to acceptable levels.

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

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References

1. Nobre, C., Vilarinho, C., Alves, O., Mendes, B., Gonçalves, M.: Upgrading of refuse derived fuel through torrefaction and carbonization: evaluation of RDF char fuel properties. *Energy* **181**, 66–76 (2019)
2. Haykiri-Acma, H., Kurt, G., Yaman, S.: Properties of biochars obtained from RDF by carbonization: influences of devolatilization severity. *Waste Biomass Valorization* **8**(3), 539–547 (2016). <https://doi.org/10.1007/s12649-016-9610-5>
3. Recari, J., Berruco, C., Puy, N., Alier, S., Bartrolí, J., Farriol, X.: Torrefaction of a solid recovered fuel (SRF) to improve the fuel properties for gasification processes. *Appl. Energy* **203**, 177–188 (2017)
4. Oliveira, I., Blöhse, D., Ramke, H.G.: Hydrothermal carbonization of agricultural residues. *Bioresour. Technol.* **142**, 138–146 (2013)
5. Poudel, J., Ohm, T., Lee, S., Oh, S.: A study on torrefaction of sewage sludge to enhance solid fuel qualities. *Waste Manag.* **40**, 112–118 (2015)
6. Chen, W.T., Haque, M.A., Lu, T., Aierzhati, A., Reimonn, G.: A perspective on hydrothermal processing of sewage sludge. *Curr. Opin. Environ. Sci. Heal.* **14**, 63–73 (2020)
7. Shen, Y.: Dechlorination of poly(vinyl chloride) wastes via hydrothermal carbonization with lignin for clean solid fuel production. *Ind. Eng. Chem. Res.* **55**(4), 11638–11644 (2016)
8. Huang, N., Zhao, P., Ghosh, S., Fedyukhin, A.: Co-hydrothermal carbonization of polyvinyl chloride and moist biomass to remove chlorine and inorganics for clean fuel production. *Appl. Energy* **240**, 882–892 (2019)
9. Hosokai, S., Matsuoka, K., Kuramoto, K., Suzuki, Y.: Modification of Dulong’s formula to estimate heating value of gas, liquid and solid fuels. *Fuel Process. Technol.* **152**, 399–405 (2016)
10. Zhang, X., Zhang, L., Li, A.: Co-hydrothermal carbonization of lignocellulosic biomass and waste polyvinyl chloride for high-quality solid fuel production: Hydrochar properties and its combustion and pyrolysis behaviors. *Bioresour. Technol.* **294**, 122113 (2019)
11. Zhao, X., Zhan, L., Xie, B., Gao, B.: Products derived from waste plastics (PC, HIPS, ABS, PP and PA6) via hydrothermal treatment: Characterization and potential applications. *Chemosphere* **207**, 742–752 (2018)
12. Chen, W., et al.: Progress in biomass torrefaction: principles, applications and challenges. *Pro. En. Comb. Sci.* **82**, 100887 (2021)



Application of a Pine Tree in the Evaluation of Environmental Thermal Conditions

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Abstract. This article presents a method of evaluating the thermal environmental conditions of a tree, represented by a maritime pine, taking into account the surrounding external environmental conditions. Particularly, the levels of moisture content existing in the different elements of the tree (trunks, branches and leaves) are evaluated according to the conditions of air temperature and air relative humidity verified around them. The study was performed numerically and the results obtained were compared with the results obtained through experimental work in progress. The maritime pine geometry was obtained through a Computer Aided Design system software. The virtual maritime pine geometry was obtained from 2289 cylindrical elements. This maritime pine consists of 14 trunks, 25 branches and 2250 leaves. Numerical simulation was carried out by a proprietary research software called Hygrothermal Tree Modelling. The water circulation and energy transmission processes were considered in the numerical model. The experimental work consisted of measuring the moisture content of maritime pine leaves with a moisture analyzer. The results obtained show that the numerically predicted moisture content of the leaves is very similar to that obtained experimentally, with a relative error of 1.65%.

Keywords: Maritime pine design · Mass and energy transmission · Moisture content · Numerical simulation

1 Introduction

In order to assess the thermal response and water circulation in a tree, it is important to know the respective processes of mass and heat transmission. In these processes the water distribution, the diffusion, the transpiration and temperature phenomena are assessed.

Considering the phenomena associated to mass transmission verified in trees, the studies developed by Janott et al. [1], Wang et al. [2], Simon et al. [3], and Green et al. [4] present relevant models for their understanding and simulation. They can be summarized

as follows: concept of water flow in soil-plant systems [1]; a model of tree structure and functioning to include biomass production, organ sharing and water availability solutions to simulate plant and environment interaction [2]; a model to evaluate leaf temperatures and transpiration rates of trees [3]; and a soil water balance numerical model [4].

In order to predict the fire behavior and also use in fire spread models, vegetation moisture and dry matter content can be used as relevant indicators [5]. Adab et al. [5] study a set of these moisture content indices and conclude that their scaling up could be useful to apply as a previous forest fire alert system. Evaluating forest fire risk is a challenge task due to several uncertainties such as fuel flammability and ignition potential [6]. The application of moisture content indices, their implications, challenges and details of use in this type of forecast can be analyzed in the works of Rao et al. [6], Lifang et al. [7] and Nolan et al. [8].

The model of water transfer, used in the study presented in this paper, includes the distribution, diffusion and transpiration processes. This model was developed from models of blood and water flow processes in the human body [9, 10].

The mesh generation is important to assess the temperature distribution and to characterize the thermal phenomena (by conduction, evaporation, radiation and convection) occurred in the tree. The mesh generation theory implemented in the presented study is based on the mesh generation theory used to obtain the geometry of a vehicle, building or human body, used to calculate the radiative exchanges [11, 12].

The thermal response model of the maritime pine used in this work is based on thermal and radiative numerical models applied to other type of geometries, such as buildings [13] and vehicles [14].

The purpose of this work is to validate the sub-model of the Hygrothermal Tree Modelling numerical model used to calculate the moisture content in the several elements (mostly in the leaves) of a tree. In this sense, experimental results of the moisture content of maritime pine leaves were obtained, which will be used in the comparison with the results obtained numerically, assuming similar environmental conditions.

2 Numerical Model

The numerical model is based on a system of equations of mass and energy transmission. In the definition of the energy transmission equations are considered the conduction, convection, radiation and transpiration phenomena. In the definition of the mass transmission equations are considered the water mass evaluation, the water distribution, and the processes of diffusion and transpiration.

The maritime pine three-dimensional (3D) geometry model is constituted by cylindrical elements used to define the trunks, branches and leaves. The dimensions of each cylindrical element are given by its length and diameter, which is made up of several layers. This 3D geometry model will be an input of the tree thermal response numerical model.

The tree thermal response numerical model is based on the human thermal response numerical model [15], dismissing the thermoregulatory system and creating new pathways for water circulation.

The tree thermal response numerical model considers a set of balance integral equations of:

- Energy for the maritime pine body tissues;
- Mass for the water in the maritime pine.

The solution of the above system of equations is found using the Runge-Kutta-Fehlberg algorithm with error control.

The tree thermal response numerical model assumes the following phenomena:

- Heat conduction verified between the several layers of each tree element;
- Heat convection verified between the external surface of the bodies and the surrounding air environment;
- Heat evaporation, considering simultaneously the mass and heat transfer and the water phase change, verified between the external surface of the bodies and the surrounding air environment.

The following phenomena are considered in the mass transmission:

- Water distribution: the water is transported from the trunk to the branches and leaves;
- Water diffusion: water is transported within the trunk from the internal tissues to the external tissues; in this calculation, the cylindrical elements that form the trunk are divided into several layers (one inner, one outer, and a set of central layers located between them);
- Water transpiration: water is evaporated by convection from the outer layer to the environment, considering evaporative phenomena.

3 Methodology

The virtual maritime pine model (Fig. 1) has a height of 1.8 m and consists of 2289 cylindrical elements spread over two levels. Each level has 7 trunks and 12 branches. At the top of the tree there is also a branch. Finally, each branch has 90 leaves. Figure 1 shows the meshing of the tree from a side view. Figure 2 shows the meshing of the tree from a top perspective. Figure 3 shows the meshing of a branch with its leaves.

The numerical simulation has the following input data:

- Average temperature of the air surrounding the tree: 20 °C;
- Average relative humidity of the air surrounding the tree: 47%;
- Average wind speed: 5 m/s.

The numerical simulation has the following output data: average surface temperature in each element of the tree; average moisture content in each element of the tree. These values are obtained for a steady-state regime.

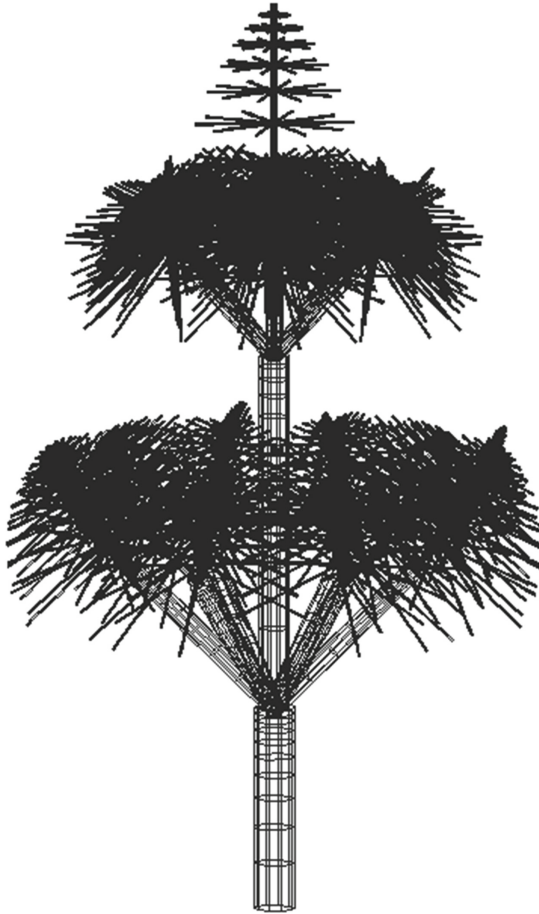


Fig. 1. Geometry of the virtual maritime pine: side view.

The experimental work requires the periodic collection of a sample of maritime pine leaves. This sample is transported to the laboratory in a closed environment. Moisture content measurement is performed using a Kern moisture analyzer. During this process, the temperature of the air and the relative humidity of the air where the collection took place are also measured.

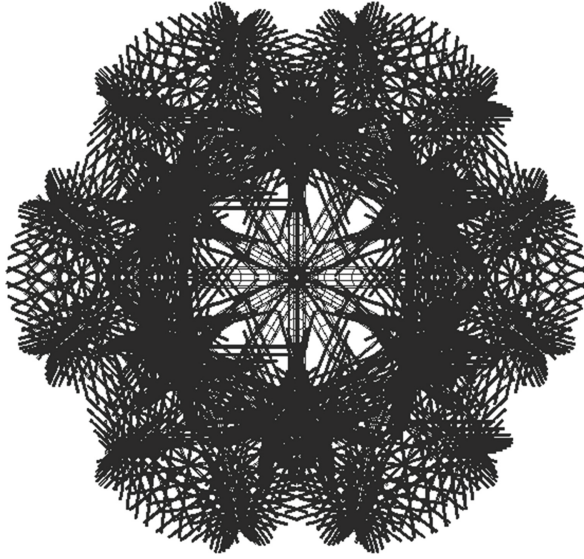


Fig. 2. Geometry of the virtual maritime pine: top view.

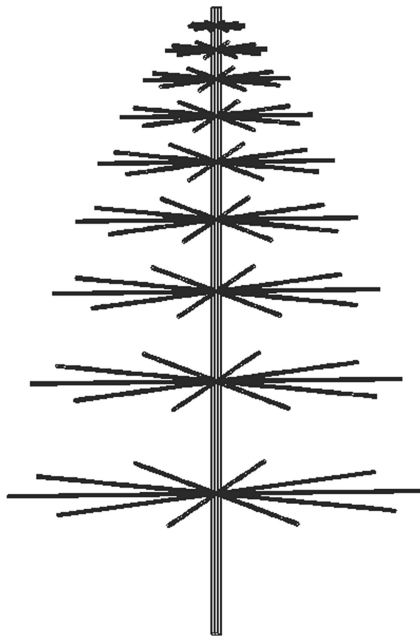


Fig. 3. Geometry of the virtual maritime pine: branch with its leaves.

4 Results and Discussion

The experimental data obtained are shown in Table 1. Five measurements of the moisture content of maritime pine leaves were considered in which the environmental conditions, given by the air temperature and air relative humidity, are similar to those used in the numerical simulation.

Table 1. Experimental data obtained for five measurements of the moisture content of maritime pine leaves.

Measurement	Moisture content (%)	Air temperature (°C)	Air relative humidity (%)
1	53.40	19.30	47.00
2	52.06	19.30	53.00
3	53.59	20.00	40.00
4	54.30	20.90	55.00
5	54.51	20.60	41.00
Average	53.57	20.02	47.20

The numerical data obtained are shown in Table 2. This table shows the moisture content obtained in the different elements of the tree according to their distribution by levels.

Table 2. Numerical data obtained for the moisture content of the different elements of the maritime pine. L means level.

Element	Moisture content (%)	Air temperature (°C)	Air relative humidity (%)
Trunks L1	53.29	20	47
Trunks L2	53.29		
Branches L1	53.70		
Branches L2	53.75		
Branch Top	53.75		
Leaves	54.46		

The results obtained show a good agreement between the results obtained experimentally and numerically. It is verified that the relative error obtained in the calculation of the moisture content of the leaves was 1.67% and in the calculation of the moisture content (average value) of the trunks/branches was -0.17%. Therefore, it can be concluded that the numerical model implemented in the calculation of the moisture content in a tree is validated.

5 Conclusions

This article presented a numerical model used to evaluate the moisture content existing in the several elements (trunks, branches and leaves) of a maritime pine, considering the surrounding external environmental conditions given by air temperature and air relative humidity. The results obtained numerically were compared with experimental measurements carried out under similar environmental conditions.

The main conclusion obtained is that the numerical model proposed for the calculation of moisture content in the tree allows obtaining numerical results similar to those obtained experimentally. Comparing these results, relative errors of -0.17% were verified for those obtained in the trunks/branches and 1.67% for those obtained in the leaves.

The model presented here is part of a broader model that has been developed over the last few years, whose main objective is to be able to determine, based on external environmental conditions, the extent of damage to a tree and its probability of survival in the face of a forest fire. Therefore, it will be possible to define protection strategies that increase their resistance to forest fires.

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References

1. Janott, F., Gayler, S., Gessler, A., Javaux, M., Klier, C., Priesack, E.: A one-dimensional model of water flow in soil-plant systems based on plant architecture. *Plant Soil* **341**, 233–256 (2011)
2. Wang, F., et al.: A functional and structural Mongolian Scots pine (*Pinus sylvestris* var. *mongolica*) model integrating architecture, biomass and effects of precipitation. *PLoS ONE* **7**(8), 43531 (2012)
3. Simon, H., Lindén, J., Hoffmann, D., Braun, P., Bruse, M., Esper, J.: Modeling transpiration and leaf temperature of urban trees – a case study evaluating the microclimate model ENVI-met against measurement data. *Landsc. Urban Plan.* **174**, 33–40 (2018)
4. Green, S., Vogeler, I., Clothier, B., Mills, T., Dijssel, C.: Modelling water uptake by a mature apple tree. *Aust. J. Soil Res.* **41**, 365–380 (2003)
5. Adab, H., Kanniah, K., Beringer, J.: Estimating and up-scaling fuel moisture and leaf dry matter content of a temperate humid forest using multi resolution remote sensing data. *Remote Sens.* **9**, 961 (2016)
6. Rao, K., Williams, A., Flefil, J., Konings, A.: SAR-enhanced mapping of live fuel moisture content. *Remote Sens. Environ.* **245**, 111797 (2020)
7. Chen, L., Dou, Q., Zhang, Z., Shen, Z.: Moisture content variations in soil and plant of post-fire regenerating forests in central Yunnan Plateau, Southwest China. *J. Geog. Sci.* **29**(7), 1179–1192 (2019). <https://doi.org/10.1007/s11442-019-1652-8>
8. Nolan, R., et al.: Linking forest flammability and plant vulnerability to drought. *Forests* **11**, 779 (2020)
9. Conceição, E., Awbi, H.: Evaluation of integral effect of thermal comfort, air quality and draught risk for desks equipped with personalized ventilation systems. *Energies* **14**(11), 3235 (2021)

10. Conceição, E., Lúcio, M., Farinho, J.: Experimental and numerical study of personalized of ventilation in classrooms desks. In: Proceedings of 10th International Conference on Air Distribution in Rooms, ROOMVENT 2007, Helsinki, Finland, 13–15 July 2007 (2007)
11. Conceição, E., Lúcio, M.: Numerical study of the influence of opaque external trees with pyramidal shape on the thermal behaviour of a school building in summer conditions. *Indoor Built Environ.* **19**(6), 657–667 (2010)
12. Conceição, E., Nunes, A., Gomes, J., Lúcio, M.: Application of a school building thermal response numerical model in the evolution of the adaptive thermal comfort level in the Mediterranean environment. *Int. J. Vent.* **9**(3), 287–304 (2010)
13. Conceição, E., Santiago, C., Lúcio, M., Awbi, H.: Predicting the air quality, thermal comfort and draught risk for a virtual classroom with desk-type personalized ventilation systems. *Buildings* **8**(2), 35 (2018)
14. Conceição, E.Z.E., Da Silva, M.C.G., André, J.C.S., Viegas, D.X.: Thermal behaviour simulation of the passenger compartment of vehicles. *Int. J. Vehicle Design* **24**(4), 372–387 (2000)
15. Conceição, E., Lúcio, M.: Numerical and subjective responses of human thermal sensation. In: 6th Portuguese Conference on Biomedical Engineering, BIOENG'2001, Faro, Portugal, 11–12 June 2001 (2001)



Design, Thermal Response and Comfort in an Auditorium with Complex Topology

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Abstract. This article presents a numerical study on the design, thermal response and comfort level of an auditorium with a complex topology, taking into account the winter season. The design and thermal response of the auditorium are studied numerically using proprietary research software, called, respectively, Geometric Design Modeling and Buildings Thermal Response Modeling (BTRM). In addition to the thermal response in transient conditions, the BTRM software also assesses the building's interior environmental conditions, particularly the levels of air quality and thermal comfort provided to the occupants. The indoor air quality (IAQ) is determined by the concentration of carbon dioxide (CO₂). The thermal comfort is determined by the Predicted Mean Vote (PMV) index. In this study, it is considered that the auditorium, similar to a real one, has a typical occupancy cycle of a classroom and its maximum capacity of 168 occupants. Connected to the auditorium is a corridor with south-facing windows, so the possibility of this corridor being used as a passive solar greenhouse is also discussed. The results demonstrate that it is possible to guarantee acceptable levels of IAQ as established by the ASHRAE 62.1 standard for the concentration of CO₂, but without being able to reach acceptable values of the PMV index as proposed in the ISO 7730 standard.

Keywords: Geometric and thermal modeling · Indoor air quality · Thermal comfort

1 Introduction

The design and the thermal response of a real auditorium are the main focus of this numerical study. Therefore, it is important to be able to virtually generate the geometry of this auditorium so that its thermal behavior can be analyzed. The auditorium's thermal

response will make it possible to analyze its thermal comfort conditions. Thermal comfort conditions also depend on the ventilation implemented, as well as indoor air quality (IAQ) conditions.

The design is developed by a numerical model to generate the three-dimensional geometry of the auditorium. Geometric surfaces based on four lines and four points are used to generate this geometry. The calculus of the mesh in the surfaces used geometric equations in cylindrical coordinates characterized by angle, radius and z coordinates. This type of methodology was previously used, e.g., in buildings [1], and in the definition of the geometry of the human body (occupant simulation) [2]. This mesh is used to evaluate incident, transmitted and absorbed solar radiation in interior and exterior spaces, as well as heat transfer by radiation in each space [3]. The meshes on the building surfaces are also used to generate the system of integral equations of energy and mass balance.

The thermal study of occupied buildings uses the Building Thermal Modeling software to calculate the temperature and mass distributions in the different spaces and elements of the building, among other parameters [4, 5]. The thermal response of the auditorium uses a numerical model based on energy and mass balance integral equations [6]. The energy balance equations take into account the phenomena of conduction, convection, radiation and evaporation. The mass balance equations consider the phenomena of diffusion, convection and adsorption/desorption. The research software developed by the authors also included sub-models to calculate solar radiation, radiative properties of glass, energy and mass convection coefficients, airflow rate, among others. The solution of the above mentioned system of equations is obtained through the Runge-Kutta-Fehlberg method with error control. The numerical model was validated, either in a steady-state or in a transient regime, in buildings, experimental chambers and other spaces.

The thermal comfort is evaluated in this study by the Predicted Mean Vote (PMV) index. This index (and also Predicted Percentage of Dissatisfied index) was developed by Fanger [7]. PMV index depends on four indoor environmental parameters and two personal parameters [7]. The indoor environmental parameters are the air temperature, air velocity, relative humidity of the air and mean radiant temperature of the surrounding surfaces (floor, ceiling and walls). The personal parameters are the activity level and insulation clothing level. This is an index commonly used in studies involving the assessment of thermal comfort in buildings [8, 9], having been adopted by international standards such as ISO 7730 [10] to categorize thermal comfort. ISO 7730 establishes three categories of thermal comfort, A, B and C, depending on the PMV index values obtained [10]. For example, the least restricted is category C, being defined by $-0.7 \leq \text{PMV} \leq +0.7$.

IAQ usually can be evaluated by the concentration of dioxide carbon (CO_2) released during the occupant's breathing process [11–13]. The international standard ASHRAE 62.1 [14] establishes the acceptable limit of IAQ in function of the CO_2 concentration and the airflow rate of the ventilation system recommend according to the number of occupants and the activities performed by them in the different compartments of the building. The acceptable limit value recommended by this standard is 1800 mg/m^3 (1000 ppm) [14].

The main objective of this work is to evaluate the thermal comfort, in winter conditions, and the IAQ in a real auditorium existing in a university building using research software developed by the authors that simulates the geometry and the thermal response of that auditorium. In addition, the possibility of using a corridor attached to the auditorium as a passive solar greenhouse is studied. This corridor has a large glazed surface facing south, which gives it promising conditions to be used as a solar greenhouse during the winter season in the northern hemisphere, which could be a possible solution to improve thermal comfort conditions [15, 16].

The rest of the content of this paper is organized as follows: Sect. 2 gives a brief description of the numerical models used in the simulation; Sect. 3 presents the geometry of the building as well as the methodology implemented in the numerical simulation; in Sect. 4 the results are shown and discussed regarding the solar radiation obtained in the corridor and the air temperature, PMV index and CO₂ concentration obtained in the auditorium; finally, Sect. 5 presents the most relevant conclusions.

2 Numerical Model

This study uses research software developed by the authors based on two numerical models: Auditorium Geometry Design and Auditorium Thermal Modeling.

The Auditorium Geometry Design is used in the auditorium design and mesh generation. This model takes into account the following:

- Geometric equations in cylindrical coordinates (defined by the angle, radius and z coordinates) are used to develop the geometry of the auditorium and its attached corridor;
- The geometry is used to establish the mesh generation and the system of energy and mass balance integral equations;
- The mesh generation is used to calculate the view factors and the mean radiant temperature;
- The energy and mass balance integral equations are developed for each surface and space; opaque surfaces consist of several layers and transparent and inner ones consist of one layer.

The Auditorium Thermal Modeling uses the previously developed energy and mass balance integral equations to calculate the temperature, contaminants (CO₂ concentration) and water vapor distribution, the thermal comfort and IAQ levels:

- The temperature distribution is calculated in the several layers of the opaque bodies, in the layer of the transparent and inner bodies, and in the air inside the compartment;
- The thermal comfort of the occupants is assessed by the PMV index, so it depends on the air temperature, the air relative humidity and the air velocity inside the compartment, the mean radiant temperature, as well as the activity and clothing insulation levels of the occupants [7, 10];
- The IAQ depends on CO₂ concentration [14].

3 Numerical Methodology

The virtual auditorium (Fig. 1) used in the numerical simulations consists of 759 opaque bodies and 25 transparent bodies (Fig. 2). Each surface is subdivided into at least 100 infinitesimal areas when meshing.

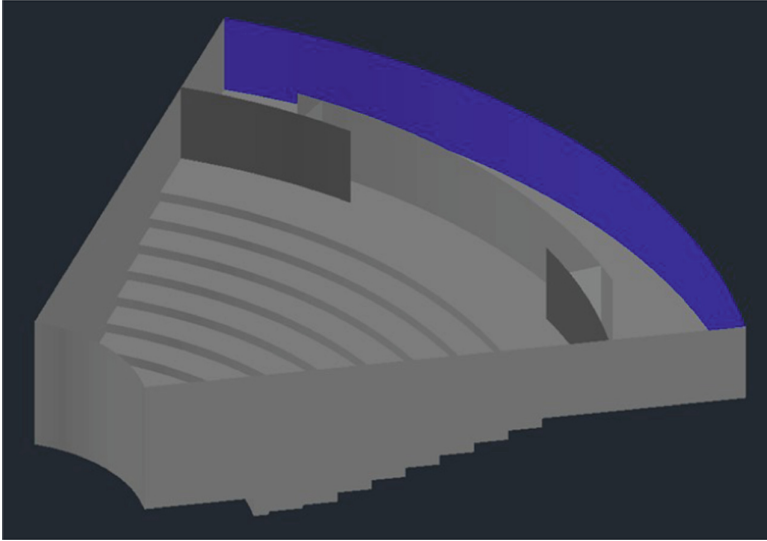


Fig. 1. Virtual auditorium used in the numerical simulation. It consists of the auditorium space for the participants and an attached corridor with a glazed surface facing south (in blue).

The auditorium built from 25 angles and 9 steps (levels) is divided as follows:

- The auditorium for participants with a maximum capacity of 168 people. This space is subject to the heat transfer from the occupants and the airflow renewal from the outside environment;
- The attached corridor with a glazed surface consisting of 25 windows facing south and with infiltrations of airflow from the outside environment;
- A connection between the auditorium and the corridor made by two doors (Fig. 1).

Numerical simulations were carried out considering winter conditions in the region of the building, whose climate is characterized by being of the Mediterranean type. Six consecutive days were simulated although only the results referring to the last day of the simulation are presented. It was considered that the auditorium was occupied by 168 people (maximum occupancy limit) in order to assess the most demanding situation from the point of view of the ventilation system.

For the purposes of the simulation, it was considered that each occupant has an average weight of 70 kg, an average height of 1.7 m, an activity level of 1.2 met and a

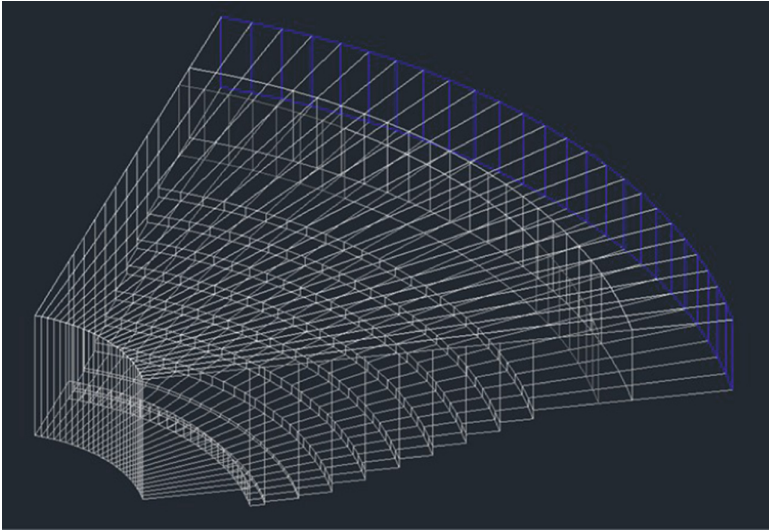


Fig. 2. Auditorium made up of 759 opaque surfaces and 25 transparent surfaces (in blue).

clothing insulation level of 1.0 clo (typical value in the winter season) [6, 10]. The occupation cycle was considered according to the typical timetable of classes in a university auditorium, that is, between 8 am and 12 pm and between 2 pm and 6 pm.

Throughout the day, the ventilation is done as follows: outside air is introduced into the auditorium with a certain airflow rate and then exhausted to the outside. The airflow rate value is a percentage of the airflow rate value recommended by the standards [14] for the people in the occupied space (168 in this study). When the auditorium is with occupation, the percentage is 75%; the rest of the time, the percentage drops to 25%. After several simulations, these values were chosen as the ones that ensure the best compromise between PMV index and CO₂ concentration values throughout the occupancy cycle.

The obtained results considered for analysis are the daily evolutions of solar radiation incident on the windows of the corridor, of the CO₂ concentration inside the auditorium, of the air temperature inside the auditorium and corridor, and of the PMV index.

4 Results and Discussion

In this work, the thermal response, in winter conditions, of a virtual auditorium similar to a real one is analyzed. The thermal response of the corridor (see Fig. 1) attached to the auditorium is also introduced in this analysis in order to assess the possibility that this corridor could later be used as a solar passive greenhouse. Note that the glazed surface of this corridor faces south, which provides positive heat gains in the winter season. So, Fig. 3 shows the daily evolution of solar radiation incident on the glazed surface (consisting of 25 windows) of the corridor. In order to assess the IAQ, it is shown in Fig. 4 the daily evolution of the CO₂ concentration in the auditorium. The thermal response of the auditorium and the attached corridor is shown here in Fig. 6 by the

daily evolution of the air temperature obtained in these spaces. Figure 5 also shows the evolution of the outside ambient air temperature in order to serve as a reference. In order to assess the thermal comfort of the occupants, it is shown in Fig. 6 the daily evolution of the PMV index in the auditorium.

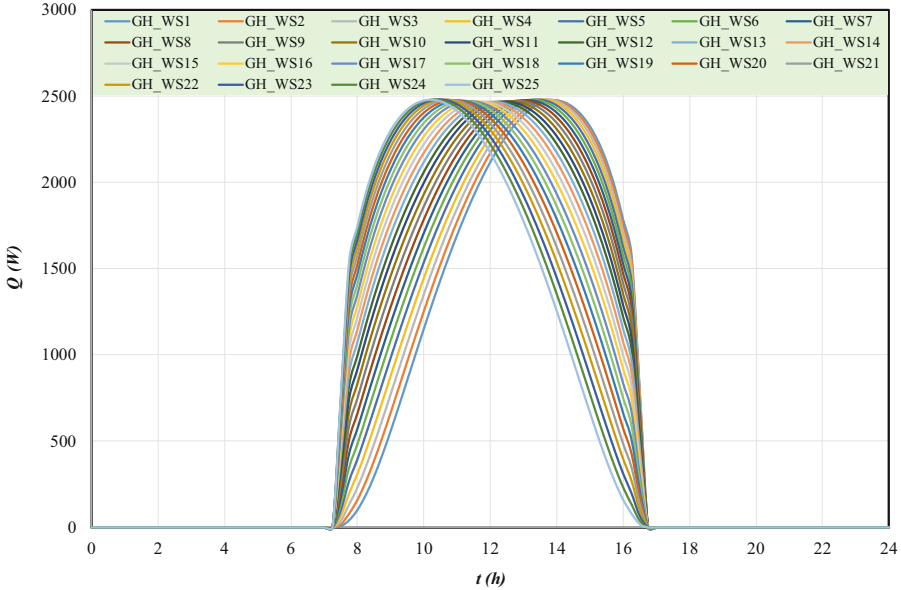


Fig. 3. Daily evolution of solar radiation incident on each of the windows of the corridor.

The incident solar radiation is similar in all windows, which have the same dimensions and the same type of glass. However, the evolution of solar radiation presents some delay between them due to the slight inclination of each window in relation to the south-facing plane.

During occupancy, the CO₂ concentration values are below the limit value of 1800 mg/m³ recommended by the standard [14], so the IAQ provided to the occupants presents an acceptable level. Furthermore, it is also confirmed that the airflow rate is also properly adjusted to the number of occupants as far as the IAQ is concerned.

During occupancy, the auditorium is under the influence of the external airflow and the heat transfer from the occupants. The indoor air temperature in the auditorium is slightly higher than the outdoor air temperature and much lower than the air temperature in the corridor. The air temperature inside the auditorium during the afternoon occupancy is higher than during the morning occupancy, with some heat accumulation, but not enough for the air temperature to reach at least 20°C. On the other hand, the relatively high temperatures reached in the corridor during the auditorium occupancy allow us to assert that the heat accumulated in this space can be used to improve the thermal conditions inside the auditorium if properly transferred.

During occupancy, the thermal comfort level of the occupants is not acceptable by negative values of the PMV index [10]. The PMV values are far from the values

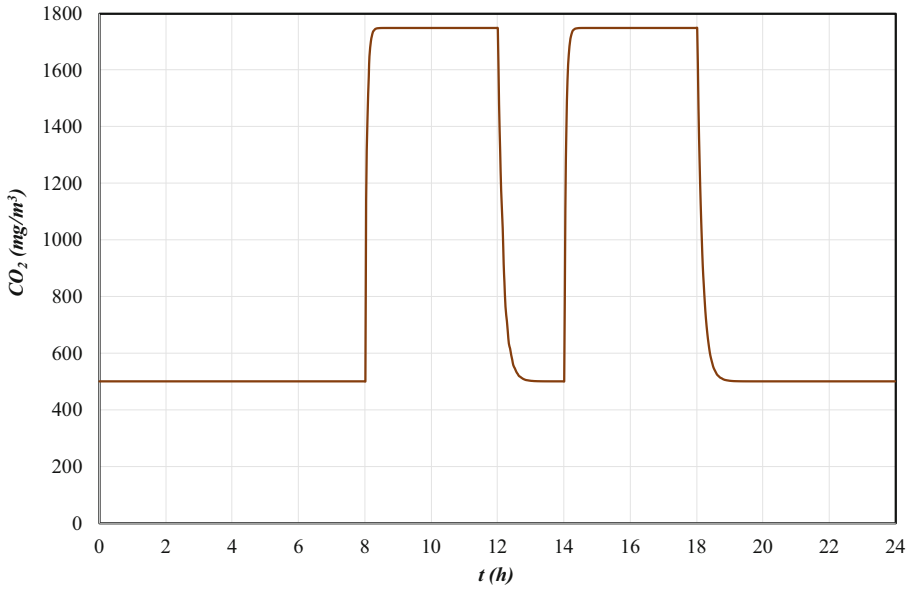


Fig. 4. Daily evolution of CO₂ concentration inside the auditorium.

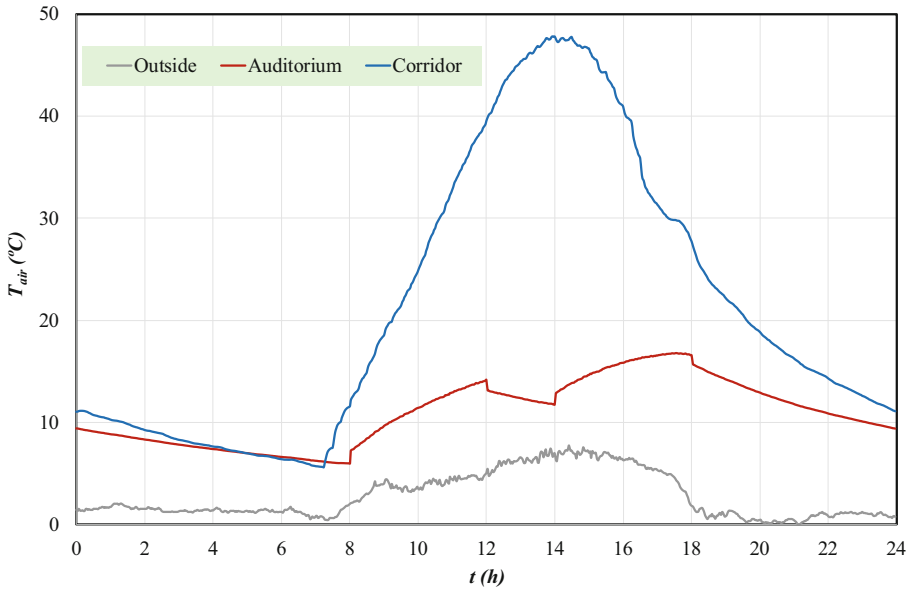


Fig. 5. Daily evolution of air temperature inside the auditorium and corridor as well as outside air temperature.

corresponding to category C of the standard [10], however they increase throughout the day, especially during occupation. This shows that the airflow rate of the ventilation

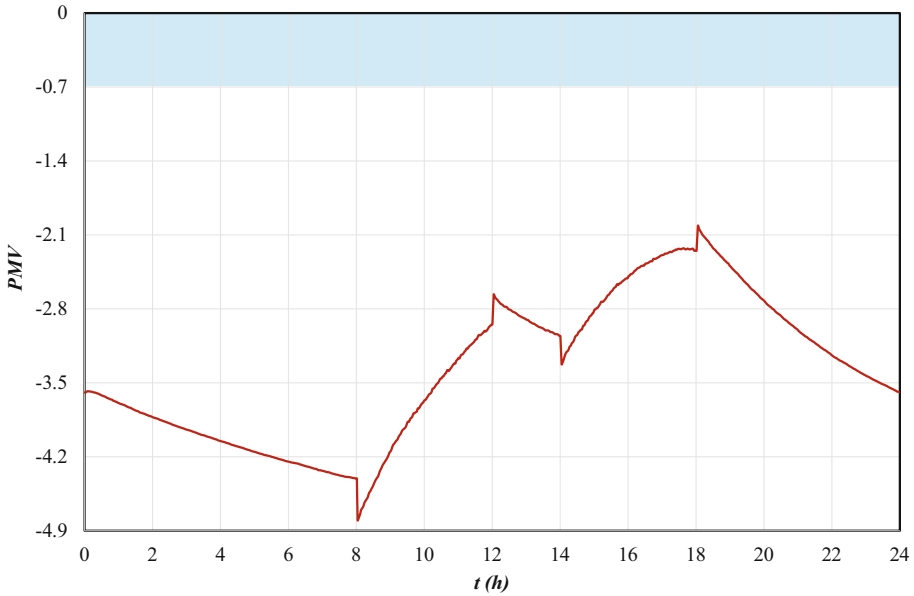


Fig. 6. Daily evolution of PMV index inside the auditorium. The shaded zone defines the thermal comfort zone by negative values of the PMV index according to Category C [10].

system is too high and should therefore be reduced, a solution that will lead to a decrease in the IAQ.

As the results show, an increase in the airflow rate decreases the concentration of CO_2 , contributing to the improvement of the IAQ, and decreases the values of the PMV index, thus worsening the thermal comfort level of the occupants. Therefore, as an alternative solution, the corridor attached to the auditorium can be used as a solar passive greenhouse to further the increase in the air temperature inside the auditorium, without jeopardizing the concentration of CO_2 inside the auditorium, as the corridor essentially serves for the movement of people during the break between classes.

5 Conclusions

The design, thermal response and comfort evaluation of an auditorium with complex topology was presented in this article. An own research software, Auditorium Thermal Modeling, was used to numerically evaluate the amount of solar radiation incident on the south-facing glazed surface of the corridor attached to the auditorium, the air temperature inside the corridor and auditorium, the thermal comfort (using PMV index) and the IAQ (using CO_2 concentration).

The results obtained show that it can be concluded that the implemented ventilation system provides an acceptable level of IAQ, but cannot guarantee an acceptable level of thermal comfort for the occupants. The CO_2 concentration is within the acceptable limit of 1800 mg/m^3 [14]. However, during occupancy, the thermal comfort level is quite far from the C category of the standard [10] due to negative values of the PMV index.

The results of the air temperature obtained inside the corridor show that this space has heating conditions conducive to improving the thermal comfort in the auditorium, which suggest its operation as a solar passive greenhouse. Thus, in the future works the airflow used in the auditorium during the occupancy will come from the corridor (operating as a solar greenhouse).

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References

1. Conceição, E., Nunes, A., Gomes, J., Lúcio, M.: Application of a school building thermal response numerical model in the evolution of the adaptive thermal comfort level in Mediterranean environment. *Int. J. Vent.* **9**(3), 287–304 (2010)
2. Conceição, E., Santiago, C., Lúcio, M., Awbi, H.: Predicting the air quality, thermal comfort and draught risk for a virtual classroom with desk-type personalised ventilation systems. *Buildings* **8**(2), 35 (2018)
3. Conceição, E., Lúcio, M.: Numerical study of the influence of opaque external trees with pyramidal shape on the thermal behaviour of a school building in summer conditions. *Indoor Built Environ.* **19**(6), 657–667 (2010)
4. Smith, V., Sookoor, T., Whitehouse, K.: Modeling building thermal response to HVAC zoning. *ACM SIGBED Review* **9**(3), 39–45 (2012)
5. Guo, J., Zheng, W., Tian, Z., Wang, Y., Wang, Y., Jiang, Y.: The short-term demand response potential and thermal characteristics of a ventilated floor heating system in a nearly zero energy building. *J. Energy Storage* **45**, 103643 (2022)
6. Conceição, E., Gomes, J., Awbi, H.: Influence of the airflow in a solar passive building on the indoor air quality and thermal comfort levels. *Atmosphere* **10**(12), 766 (2019)
7. Fanger, P.: *Thermal Comfort: Analysis and Applications in Environmental Engineering*. Danish Technical Press, Copenhagen (1970)
8. Cheung, T., Schiavon, S., Parkinson, T., Li, P., Brager, G.: Analysis of the accuracy on PMV – PPD model using the ASHRAE global thermal comfort database II. *Build. Environ.* **153**, 205–217 (2019)
9. Fletcher, M., Glew, D., Hardy, A., Gorse, C.: A modified approach to metabolic rate determination for thermal comfort prediction during high metabolic rate activities. *Build. Environ.* **185**, 107302 (2020)
10. ISO 7730: Ergonomics of the Thermal Environments—Analytical Determination and Interpretation of Thermal Comfort Using Calculation of the PMV and PPD Indices and Local Thermal Comfort Criteria. International Standard Organization, Geneva, Switzerland, (2005)
11. Conceição, E., Silva, M., Viegas, D.: Air quality inside the passenger compartment of a bus. *J. Expo. Anal. Environ. Epidemiol.* **7**(4), 521–534 (1997)
12. Conceição, E., Farinho, J., Lúcio, M.: Evaluation of indoor air quality in a classroom equipped with crossed ventilation. *Int. J. Vent.* **11**(1), 53–67 (2012)
13. Asif, A., Zeeshan, M., Jahanzaib, M.: Indoor temperature, relative humidity and CO₂ levels assessment in academic buildings with different heating, ventilation and air-conditioning systems. *Build. Environ.* **133**, 83–90 (2018)

14. ANSI/ASHRAE Standard 62-1: Ventilation for Acceptable Indoor Air Quality, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA, USA (2016)
15. Aelenei, D., Leal, H., Aelenei, L.: The use of attached-sunspaces in retrofitting design: the case of residential buildings in Portugal. *Energy Procedia* **48**, 1436–1441 (2014)
16. Bataineh, K., Fayez, N.: Analysis of thermal performance of building attached sunspace. *Energy and Buildings* **43**(8), 1863–1868 (2011)



Towards Sustainable Seaweed Production - Optimising the Culture of *Gracilaria Gracilis*

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Abstract. *Gracilaria gracilis* is a well-known cultivated seaweed, sought after for its high agar content. For this purpose, it is one of the most cultivated species worldwide. Depending on the biotic and abiotic conditions to which it is exposed, the species also exhibits a very interesting nutritional profile, making it an excellent candidate for use as a food or food supplement. Thus, aiming to improve the productivity and biomass quality, *G. gracilis* was cultivated under different light conditions and nutrient media, to evaluate the impact of these parameters on the growth rate and the chemical composition of the biomass. Thus, the nutritional profile of the biomass was evaluated. Our results indicate that environmental parameters have a significant impact both on growth and quality of the biomass, affecting the amount of protein, ash, and carbohydrate. The cultivation methods, therefore, significantly affected the quality of the biomass produced. Thus, there is scope to optimise the cultivation of *G. gracilis*, in order to efficiently produce high quality biomass, enhancing the effective use of resources, particularly nutrients, while producing nutritionally balanced biomass for human consumption.

Keywords: Rhodophyta · Gracilarioid · Growth rate · Protein content · Carbohydrate content

1 Introduction

Seaweeds have long been used as a food source, mainly in the Asian and Indo-Pacific countries, but also in coastal populations of Europe, Mediterranean, America, and the Caribbean islands [1]. These marine organisms are consumed for their healthy content in primary and secondary metabolites, such as a high content in protein (up to 47% in red seaweeds) with a balanced content in essential amino acids, low content of lipids (but with a noteworthy proportion of polyunsaturated fatty acids), and high mineral content. They are also good sources of carbohydrates including sugars, and are rich in fibres, hydrocolloids, pigments, vitamins, polyphenols, among others [2–10]. These bioactive compounds show a beneficial effect on human health and well-being, such as antioxidant, antimicrobial, anti-inflammatory, antithrombotic effects, decrease the risk

of cardiovascular diseases, strengthen the immune defence system, and improve calcium, iron, and iodine diet deficiencies, among others [3, 11–17].

Seaweeds consumption has been increasing in recent decades worldwide, particularly in European countries. Nevertheless, European legislation limits the number of species, allowing the consumption of only a few seaweeds, namely the brown seaweeds *Ascophyllum nodosum*, *Fucus* spp., *Laminaria* spp., *Undaria pinnatifida*, the red seaweeds *Chondrus crispus*, *Gracilaria* spp. *Porphyra* spp. *Palmaria palmata*, the green seaweeds *Ulva* spp., and a few others [18].

Seaweeds aquaculture and harvesting is an extensive global industry. World seaweeds production has more than tripled from 10.6 million tonnes in 2000 to 32.4 million tonnes in 2018. Still, the number of cultivated species is small, being limited to *Saccharina japonica*, *Gracilaria* spp., *Eucheuma* spp., *Porphyra* spp., *Codium* spp., *Kappaphycus alvarezii*, and *Sargassum fusiforme* [19, 20]. Many other species are still harvested from wild populations. Just to name a few, *Gelidium corneum* and *Pterocladia capillacea* are harvested for the extraction of agar, *Mastocarpus stellatus* and *Chondrus crispus* are harvested for the extraction of carrageenans, and *Laminaria hyperborea* is harvested for the extraction of alginates [19, 21, 22].

As seaweeds cultivation increases, knowledge about growth improves, especially about the importance of environmental factors [4, 23]. Among these, nutrients and light are key factors that determine the yield and productivity of the algal biomass [24]. As for pH, fluctuations in its value determine the uptake of carbon by seaweeds, because a higher pH decreases carbon availability, namely dissolved inorganic carbon [25], which in turn decreases Rubisco activity and therefore the rate of photosynthesis, due to the enzyme's low affinity for CO₂ [26].

One of the most cultivated species worldwide is *Gracilaria gracilis* used as industrial food-grade agar, but also as food, and for medical purposes [3, 27]. In fact, the species has a remarkably interesting nutritional profile, as stated in previous works, but with evident seasonal variations, as is common in Gracilarioids [4, 28–30]. As to bioactivities, Torres et al. review paper [31] states more than 400 papers researching *Gracilaria* spp. Many properties. Thus *Gracilaria* spp. is one of the most interesting seaweeds to be used as food or supplement, to improve health and wellbeing.

In this study we aim to determine the chemical composition of *Gracilaria gracilis*, grown under different conditions (light, pH, nutrient source), to evaluate the impact of these different laboratory growth conditions. The data gathered will allow optimizing laboratory conditions for *G. gracilis* to increase productivity and decrease costs, while improving the quality of the biomass as a food source.

2 Material and Methods

2.1 Sample Preparation

Gracilaria gracilis (Stackhouse) Steentoft, L.M. Irvine & Farnham 1995 (Rhodophyta) biomass used in this study was grown from spores, shed by fully matured female fronds harvested in 2019 from Buarcos (40°9'57"N, 8°53'5"W), Portugal, according to Freitas et al. [28]. Since then, the seaweeds were cultivated from thalli tips, in constantly aerated filtered seawater (31–35 psu) in 2 L flat-bottom flasks, in a climatic room (20 ± 1 °C). The

photoperiod was set at 16:08 (Light:Dark), with irradiance being provided by daylight cool white fluorescent lamp (OSRAM Lumilux Skywhite). Cultivations were weekly supplied with full-strength Von Stosch Enriched (VSE) modified culture media, adapted for red seaweed use [32]. Germanium dioxide (GeO_2) was also added to the medium (1 mL L^{-1}) to prevent the growth of diatoms.

2.2 Culture Methods

For each assay, fifteen healthy tips were randomly selected, weighted and distributed throughout 250 mL flat-bottom flasks in the climatic room set at $20 \pm 1 \text{ }^\circ\text{C}$. Different assays were performed, as summarized in Table 1. The control growth conditions were set for Assay A, with seawater at $\text{pH} = 7$ supplied with VSE medium and white cool fluorescent light ($20 \pm 0.5 \text{ } \mu\text{mol photons m}^{-2} \text{ s}^{-1}$, OSRAM Lumilux Skywhite). Two sets of three flasks were used for the control ($n = 6$). In assay B the medium used was Acadian™ Soluble Seaweed Extract Powder (SSEP) culture media. In assay C a $\text{pH} = 9$ was considered and in assay D the light source used was white LED ($20 \pm 0.5 \text{ } \mu\text{mol photons m}^{-2} \text{ s}^{-1}$, Ywaio T8 LED Tube Light). Three flasks were used per each nutrient media, pH, and light source ($n = 3$), all placed under a photoperiod of 16:8 and constant aeration. All assays lasted for 2 weeks.

Table 1. Summary of *Gracilaria gracilis* growth assays performed.

Assay	Light	pH	Culture media
A	White cool florescent	7	VSE modified medium
B	White cool florescent	7	Acadian™ SSEP
C	White cool florescent	9	VSE modified medium
D	White LED	7	VSE modified medium

2.3 Growth Measurements

Biomass weight was recorded prior to and at the end of each trial in a small-scale (Sartorius TE124S – $120 \text{ g} \times 0.0001 \text{ g}$). The water excess was gently removed with paper towels before weighting. Relative Growth Rate (RGR) calculations were performed according to Patarra et al. [33]:

$$\text{RGR (\% fw day}^{-1}\text{)} = \frac{\ln(fw) - \ln(iw)}{t} \times 100 \quad (1)$$

The iw and fw stand, respectively, as initial, and final weights expressed in gram, and t stands as time in days of the trial duration.

2.4 Proximate Composition

Moisture and ash contents were determined according to the official AOAC standard methods [34], as was total protein content determination by the Kjeldahl method, estimated using a conversion factor of 5 specific to red seaweeds [35]. The total carbohydrate content was determined using an adaptation of the method of Dubois et al. [36]. Lipid content was determined using the Folch method [37] with modifications.

2.5 Statistical Analysis

All assays were tested through a one-way Analysis of Variance (ANOVA), preceded by normality and homogeneity of variance validation to meet the assumptions of parametric statistical analysis. Whenever homogeneity of variances was achieved, multiple comparisons tests were performed, while the non-parametric Kruskal-Wallis test was used when homogeneity of variances was not fulfilled. All differences were considered significant at p -value < 0.05 . Data were expressed as mean \pm standard deviation. Statistical differences were considered significant at p -value < 0.05 . Calculations were performed with SPSS Statistics 27 (IBM Corporation, New York, EUA).

3 Results and Discussion

3.1 Relative Growth Rate

The different growing conditions tested yielded significantly different relative growth rates (RGR) between the lights tested. Assays A (control – VSE), B (SSEP), and C (VSE with $\text{pH} = 9$), significantly produced more biomass than assay D (white LED) which showed the lowest yield with a RGR of only $2.35 \pm 0.67\% \text{ day}^{-1}$ (ANOVA, $p = 0.000$) (Fig. 1).

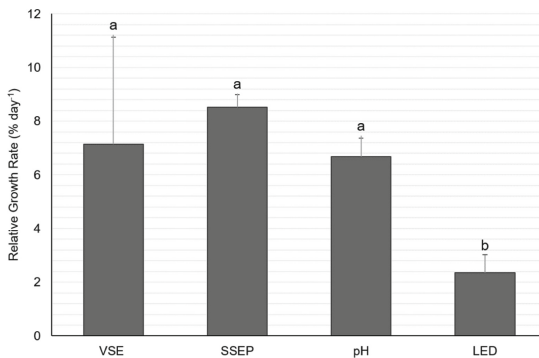


Fig. 1. Relative Growth Rate of *Gracilaria gracilis* grown under different conditions: control VSE modified medium (VSE), Soluble Seaweed Extract (SSEP), VSE medium with $\text{pH} = 9$ and with LED white light (LED). Bars represent means ($n = 3$) and letters above bars pinpoint RGR statistical differences between growth conditions ($p < 0.05$).

It should also be noted that the assay B (SSEP), although not statistically significant ($p > 0.05$), presented appreciable growth rate, compared to the assay A (control-VSE), respectively 8.15 ± 0.48 and $7.15 \pm 3.97\%$. RGR dictates the feasibility of efficiently producing high biomass yields to maximize profits from their commercialization. Our results show that, within our trials, the main abiotic factor affecting the growth of *G. gracilis* was the type of light in which the algae were grown. Mensi and Ghedifa [38] noted that an increase in light intensity could cause a reduction in the efficiency of photosynthesis due to the possibility of photooxidation, occurring when excessive light causes the destruction of photosystem II, which is sensitive to a wide range of environmental conditions [39]. Thus, photooxidation reactions inside the cell decrease growth, or under extreme stress condition even induce death.

Although not significantly different, the results obtained with the SSEP were high (RGR = $8,514\% \text{ day}^{-1}$) when compared to control VSE (RGR = $7,152\% \text{ day}^{-1}$) and VSE at pH = 9 (RGR = $6,680\% \text{ day}^{-1}$). These RGR values are higher than those obtained by Wu et al. [39] who obtained a maximum RGR of $6\% \text{ day}^{-1}$ for *Gracilariopsis lemaneiformis* (former *Gracilaria lemaneiformis*), and similar to those recorded for *G. birdiae*, by Bezerra & Marinho-Soriano [40] (Maximum RGR $7.45\% \text{ day}^{-1}$). The VSE formula contains several important nutrients such as the macronutrients ammonia and phosphate, the micronutrients iron and manganese, and the vitamins biotin, thiamine, and B12 [28]. However, VSE is highly expensive and time-consuming to prepare, and therefore unsuitable on a commercial scale [41], so, alternatives are mostly desirable. It is of utmost importance achieving better results with a different commercial medium such as SSEP, as these results show that it may contain important nutrients that benefit *G. gracilis* growth. Similar results were observed by Ali et al. [42] in which *Ascophyllum* marine plant extract enriched with potassium (AMPEP K⁺), applied to *Kappaphycus alvarezii* showed higher growth than the strains without the extract. These commercial seaweed extracts thus, seem to be an interesting alternative to laboratory made nutrient media.

3.2 Proximate Composition

As to the proximate composition of *Gracilaria gracilis*, several statistical differences can be found. In general, the obtained biomass showed high moisture values of the fresh biomass. The moisture is significantly lower in the LED assay (ANOVA, $p = 0.000$), when compared to the other assays ($75.41 \pm 1.51\%$) with moisture values higher than 85% (VSE 85.5%, SSEP 86.15 and pH 85.8%). In other words, the LED assay showed a significantly higher yield than that of the other assays, with 24.59%.

As to ash measured as percentage of dry weigh (% dw), our results also show high ash content, but without significant variations ($p > 0.05$). The LED assay presented the lowest value ($28.28 \pm 9.005\%$), the SSEP assay showed the highest ash content ($46.96 \pm 2.05\%$), followed by the pH assay ($36.35 \pm 1.72\%$) and the control (VSE) assay ($34.20 \pm 2.43\%$) (Fig. 2a). The protein content (% dw) varied between assays, ranging from $16.13 \pm 0.31\%$ in the control to $19.62 \pm 0.11\%$ in the SSEP assay. These percentages are statistically different (Kruskal-Wallis, $p = 0.016$). As for the other two assays, the protein content was intermediate, with a dry weight percentage of about 18% (Fig. 2b). The total carbohydrates are intermediate to low, but with significant variations

between assays (Fig. 2c). The lowest value was registered for the control with $12.66 \pm 0.20\%$. This value is significantly lower than the percentages obtained for the SSEP assay ($21.44 \pm 2.33\%$) and the LED assay ($19.73 \pm 3.50\%$) (ANOVA, $p = 0.009$, $p = 0.028$, respectively). The pH assay showed an intermediate value of $16.52 \pm 1.63\%$, with no statistically significant differences to the other assays ($p > 0.05$).

Finally, the total lipid content is always extremely low, as often occurs in seaweeds. Results from ANOVA test analysis showed that the lipid content of the biomass cultivated under SSEP assay is significantly lower than all the other samples (ANOVA, $p = 0.003$), with values ranging from $0.28 \pm 0.03\%$ for SSEP assay to $0.40 \pm 0.03\%$ for LED assay (Fig. 2d).

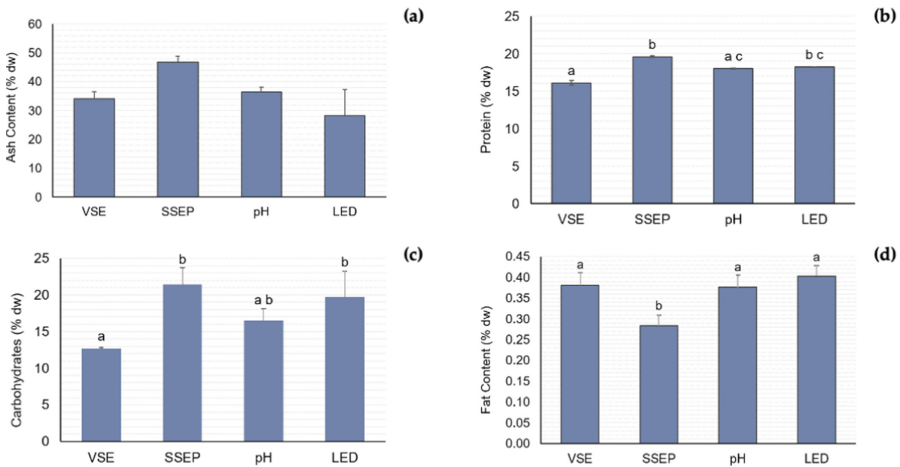


Fig. 2. (a) ash, (b) protein, (c) carbohydrates, and (d) fat contents of *Gracilaria gracilis* grown under different conditions: control VSE modified medium, (SSEP) Soluble Seaweed Extract Powder, VSE medium with pH = 9, and VSE with LED white light (LED). Bars represent means ($n = 3$) and letters above bars pinpoint statistical differences ($p < 0.05$).

With regard to moisture our results follow the pattern of other seaweeds with high moisture content [33]. As to the ash content, it is directly associated with the mineral content in seaweeds, giving a rough estimate of its content in the algae biomass. The LED assay exhibited the lowest value ($28.28 \pm 9.005\%$) and quite similar to the values obtained by our previous work and by other authors [28, 29, 43], while SSEP assay possessed the highest ash content with $46.96 \pm 2.05\%$. These high ash values are usually recorded for brown seaweeds, which are known to hold the highest mineral content among seaweeds [1]. These results may arise from the additional mineral content in SSEP medium, and its ability to hold mixtures of enriched trace metal in a soluble form [44], which can easily be incorporated into the growing *G. gracilis* biomass. As to the protein content, the SSEP and VSE control trials highest and lowest protein content are comparable to those found by Francavilla et al. [30] for *G. gracilis* and for red seaweeds in general. As we have found in our previous work, the protein content of cultivated biomass is rather high when compared to the wild biomass [28], meaning that the nutrient

culture media provide plentiful nitrogen required for the protein synthesis. Again, the composition of the SSEP medium seems to show a better fit, not only in growth but also in changing the biochemical composition of the biomass, which is most desirable from a nutritional and economic value perspective. The carbohydrate content was lower than that usually obtained for red seaweeds [1], and lower than in our previous work, when we achieved values 38% in the cultivated biomass [28]. Completing the analysis with lipidic content, all trials delivered very low percentages, as expected, since seaweeds generally have a very low lipid content [1, 3]. The values currently obtained are even lower than those found by Neto et al. [29].

Therefore, these results demonstrated that the SSEP medium could produce a high protein and extremely low-fat algae which may contribute for the development of a low energy and healthy product, worthy of being incorporated into the human diet.

4 Conclusions

Seaweed cultivation is a rewarding growing activity, that aims to provide the market with sustainable and efficient biomass production. However, optimization of the cultivation process is still required to ensure not only the highest yields but also the best quality of the biomass.

The replacement of traditional cold fluorescent white light sources by white LED sources did not prove to be an interesting alternative, probably due to different absorption peaks of photon emissions. Further studies with different LED lights, may produce better results according to the wavelengths of the emitted light. This is something worth exploring, as LED sources are currently being regarded as a worthy alternative to traditional lighting in indoor seaweed cultivation, as it is an economic and efficient technology. Changing the pH has also not proven to be an efficient method to produce better quality biomass.

However, progress towards successful *Gracilaria gracilis* production is presented, by replacing the common laboratory Von Stosch Enriched modified medium with a commercial Acadian™ Seaweed Soluble Extract Powder Medium, which has proven to increase not only seaweeds relative growth rate, but also significantly improve protein, carbohydrates, and ash content of the cultured biomass. Thus, this commercial medium appears to be very advantageous from a nutritional and economical perspective, not only because it is readily prepared, but because its composition significantly improves the algal biomass.

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References



1. Pereira, L.: Edible seaweeds of the world. In: Pereira, L., (Ed.) 1st edn. CRC Press, Boca Raton (2016). ISBN 9781498730471
2. Pereira, L.: A review of the nutrient composition of selected edible seaweeds. In: Pomin, V.H., (Ed.) Seaweed: Ecology, Nutrient Composition and Medicinal Uses, p. 248. Nova Science Publishers, UK (2011). ISBN 0250-832X (Print)n0250-832X (Linking)
3. Burtin, P.: Nutricional value of seaweeds. *Electron. J. Environ. Agric. Food Chem.* **2**, 498–503 (2003)
4. Afonso, C., Correia, A.P., Freitas, M.V., Baptista, T., Neves, M., Mouga, T.: Seasonal changes in the nutritional composition of Agarophyton vermiculophyllum (Rhodophyta, Gracilariales) from the center of Portugal. *Foods* **10**, 1145 (2021)
5. Cavaco, M., et al.: Seasonal nutritional profile of Gelidium corneum (Rhodophyta, Gelidiaceae) from the center of Portugal. *Foods* **10**, 2394 (2021). <https://doi.org/10.3390/foods10102394>
6. Lopes, G., et al.: Sterol profiles in 18 macroalgae of the Portuguese coast. *J. Phycol.* **47**, 1210–1218 (2011)
7. Valentão, P., Trindade, P., Gomes, D., Guedes de Pinho, P., Mouga, T., Andrade, P.B.: Codium tomentosum and plocamium cartilagineum: chemistry and antioxidant potential. *Food Chem.* **119**, 1359–1368 (2010)
8. Macartain, P., Gill, C.I.R., Brooks, M., Campbell, R., Rowland, I.R.: Nutritional value of edible seaweeds. *Nutrition Rev.* **65**, 535–543 (2007)
9. Cavaco, M., Duarte, A., Bernardino, S., Afonso, C., Mouga, T.: sustainable use of seaweeds from S. Martinho do Porto, Portugal – Past, Present, and future perspective. In: daCostaSanchesGalvão, J.R., et al. (eds.) Proceedings of the 1st International Conference on Water Energy Food and Sustainability (ICoWEFS 2021), pp. 216–226. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-75315-3_26
10. Bocanegra, A., Bastida, S., Benedi, J., Rodenas, S., Sanchez-Muniz, F.J.: Characteristics and nutritional and cardiovascular-health properties of seaweeds. *J. Med. Food.* **12**, 236–258 (2013)
11. Wells, M.L., et al.: Algae as nutritional and functional food sources: revisiting our understanding. *J. Appl. Phycol.* **29**(2), 949–982 (2016). <https://doi.org/10.1007/s10811-016-0974-5>
12. Mohamed, S., Hashim, S.N., Rahman, H.A.: Seaweeds: a sustainable functional food for complementary and alternative therapy. *Trends. Food. Sci. Technol.* **23**, 83–96 (2012)
13. De JesusRaposo, M.F., De Morais, A.M., De Morais, R.M.: Marine polysaccharides from algae with potential biomedical applications. *Mar. Drugs.* **13**, 2967–3028 (2015)
14. Yang, C., et al.: Anti-diabetic effect of oligosaccharides from seaweed Sargassum confusum via JNK-IRS1/PI3K signalling pathways and regulation of gut microbiota. *Food Chem. Toxicol.* **131**, 110562 (2019)
15. Pádua, D., Rocha, E., Gargiulo, D., Ramos, A.A.: Bioactive compounds from brown seaweeds: phloroglucinol, fucoxanthin and fucoidan as promising therapeutic agents against breast cancer. *Phytochem. Lett.* **14**, 91–98 (2015)
16. Wijesinghe, W.A., Jeon, Y.J.: Biological activities and potential industrial applications of fucose rich sulfated polysaccharides and fucoidans isolated from brown seaweeds: a review. *Carbohydr. Polym.* **18**, 13–20 (2012)
17. Anderson, T.; Dhandapani, R.: 37 FAMES including Omega-3 and -6 Fatty Acids, by GC-FID in Under 12 Minutes. www.phenomenex.com
18. EU: Novel Food Catalog (2022). https://webgate.ec.europa.eu/fip/novel_food_catalogue/#. 27 Feb 2022

19. Araújo, R., et al.: Current Status of the Algae Production Industry in Europe: An Emerging Sector of the Blue Bioeconomy. *Front. Mar. Sci.* **7**, 626389 (2021)
20. FAO The State of World Fisheries and Aquaculture 2020; FAO, Rome, Italy (2020). ISBN 9789251326923
21. Kraan, S.: Algal Polysaccharides, Novel Applications and Outlook. In: Chang, C.F., (Ed.) *Carbohydrates - Comprehensive Studies on Glycobiology and Glycotechnology*, pp. 489–532. InTech Open Science, Croatia, Rijeka (2012)
22. Stephen, A.M., Phillips, G.O., Williams, P.A.: *Food Polysaccharides and Their Applications*, 2nd edn. CRC Press, Boca Raton (2006)
23. Hafting, J.T., et al.: Prospects and challenges for industrial production of seaweed bioactives. *J. Phycol.* **51**, 821–837 (2015)
24. Harrison, P.J., Hurd, C.L.: Nutrient physiology of seaweeds: application of concepts to aquaculture. *Cah. Biol. Mar.* **42**, 71–82 (2001)
25. Cornwall, C.E., et al.: Carbon-use strategies in macroalgae: differential responses to lowered pH and implications for ocean acidification. *J. Phycol.* **48**, 137–144 (2012)
26. Israel, A., Hophy, M.: Growth, photosynthetic properties and Rubisco activities and amounts of marine macroalgae grown under current and elevated seawater CO₂ concentrations. *Glob. Chang. Biol.* **8**, 831–840 (2002)
27. Gioele, C., Marilena, S., Valbona, A., Nunziacarla, S., Andrea, S., Antonio, M.: *Gracilaria gracilis*, source of agar: a short review. *Curr. Org. Chem.* **21**, 380–386 (2017)
28. Freitas, M.V., Mouga, T., Correia, A.P., Afonso, C., Baptista, T.: New insights on the sporulation, germination, and nutritional profile of *Gracilaria gracilis* (Rhodophyta) grown under controlled conditions. *J. Mar. Sci. Eng.* **9**, 562 (2021)
29. Neto, R.T., Marçal, C., Queirós, A.S., Abreu, H., Silva, A.M.S., Cardoso, S.M.: Screening of *Ulva rigida*, *Gracilaria* sp., *Fucus vesiculosus* and *Saccharina latissima* as functional ingredients. *Int. J. Mol. Sci.* **19**, 2987 (2018)
30. Francavilla, M., Franchi, M., Monteleone, M., Caroppo, C.: The red seaweed *Gracilaria gracilis* as a multi products source. *Mar. Drugs.* **11**, 3754–3776 (2013)
31. Torres, P., Santos, J.P., Chow, F., dos Santos, D.Y.A.C.: A comprehensive review of traditional uses, bioactivity potential, and chemical diversity of the genus *Gracilaria* (Gracilariales, Rhodophyta). *Algal Res.* **37**, 288–306 (2019)
32. Redmond, S., Green, L., Yarish, C., Kim, J., Neefus, C.: *New England Seaweed Culture Handbook*; Redmond, S., Green, L., Yarish, C., Kim, J., Neefus, C. (Eds.) Connecticut Sea Grant CTSG-14-01: Connecticut (2014)
33. Patarra, R.F., Carreiro, A.S., Lloveras, A.A., Abreu, M.H., Buschmann, A.H., Neto, A.I.: Effects of light, temperature and stocking density on *Halopteris scoparia* growth. *J. Appl. Phycol.* **29**, 405–411 (2017)
34. AOAC Official Methods of Analysis of AOAC International. Latimer Jr., G.W. (Ed.) 20th edn. Association of Official Analytical Chemists (2016). ISBN 0935584870
35. Angell, A.R., Mata, L., de Nys, R., Paul, N.A.: The protein content of seaweeds: a universal nitrogen-to-protein conversion factor of five. *J. Appl. Phycol.* **28**(1), 511–524 (2015). <https://doi.org/10.1007/s10811-015-0650-1>
36. Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F.: Colorimetric method for determination of sugars and related substances. *Anal. Chem.* **28**, 350–356 (1956)
37. Folch, J., Lees, M., Sloane Stanley, G.H.A.: simple method for the isolation and purification of total lipides from animal tissues. *J. Biol. Chem.* **226**, 497–509 (1957)
38. Fethi, M., Ghedifa, A.: Ben optimum ranges of combined abiotic factor for *Gracilaria gracilis* aquaculture. *J. Appl. Phycol.* **31**, 3025–3040 (2019)
39. Wu, H., Jiang, H., Liu, C., Deng, Y.: Growth, pigment composition, chlorophyll fluorescence and antioxidant defenses in the red alga *Gracilaria lemaneiformis* (Gracilariales, Rhodophyta) under light stress. *South Afr. J. Bot.* **100**, 27–32 (2015)

40. Bezerra, A.F., MarinhoSoriano, E.: Cultivation of the red seaweed *Gracilaria birdiae* (Gracilariales, Rhodophyta) in tropical waters of northeast Brazil. *Biomass Bioenergy* **34**, 1813–1817 (2010)
41. Kim, J.K., Mao, Y., Kraemer, G., Yarish, C.: Growth and pigment content of *Gracilaria tikvahiae* McLachlan under fluorescent and LED lighting. *Aquaculture* **436**, 52–57 (2015)
42. Ali, M.K.M., Critchley, A.T., Hurtado, A.Q.: The impacts of AMPEP K+ (Ascophyllum marine plant extract, enhanced with potassium) on the growth rate, carrageenan quality, and percentage incidence of the damaging epiphyte *Neosiphonia apiculata* on four strains of the commercially important carrageenoph. *J. Appl. Phycol.* **32**, 1907–1916 (2020)
43. Pereira, T., et al.: Optimization of phycobiliprotein pigments extraction from red algae *Gracilaria gracilis* for substitution of synthetic food colorants. *Food Chem.* **321**, 126688 (2020)
44. Craigie, J.S.: Seaweed extract stimuli in plant science and agriculture. *J. Appl. Phycol.* **23**, 371–393 (2011)



The Role of Public Policies in the Consolidation of Sustainable Tourism Destination: The Destination Analysis of the Historic Villages of Portugal

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Abstract. Sustainability has been gaining interest and prominence in development processes, especially tourism development, given the growing political, academic and inclusion in the main strategic documents of territorial development, and the evolution of public policies and the creation of new structures and instruments of sustainable management.

The main sustainability models and instruments have strengthened their role in the process of design and competitiveness of sustainable tourism destinations, asserting themselves in articulation with the public policies vehicles for the development of low density territories, in economic, socio-cultural and environmental terms, meeting the current and future needs of residents, economic agents and tourists.

In the context of operationalizing the Action Plan of the Historical Villages of Portugal, 2016–2020, the managing entity of the tourist destination (Historical Villages of Portugal - Tourism Development Association) has assumed the Sustainable Development Goals 2030, the domains of the Europe Strategy 2020 and the priorities of the Regional Strategy of the Centre, as guiding principles to increase the competitiveness and social cohesion of the tourist destination.

This work aims to identify and analyse the changes that are occurring in the destination Historical Villages of Portugal, arising from the effects of applying public policy guidelines and to know the dynamics and the role of territorial agents in the process of sustainable tourism development. For this purpose, a qualitative approach was used through content analysis of the main documents: Action Programme, AHP Benchmark and Evaluation Report of the Strategy of the Historic Villages of Portugal.

Keywords: Sustainability · Sustainable development goals 2030 · Europe strategy 2020

1 Introduction

Over the last decades, rural territories have been undergoing different mutations, leading in some cases to drastic changes in their functions and characteristics. Nowadays many of these territories face antagonistic development processes, on the one hand, a marked loss of their predominantly agricultural character and, on the other hand, the emergence of new dynamics to enhance their non-agricultural dimension, namely the conservation and protection of natural resources and biodiversity, in the management of space, and in the preservation of historical and cultural heritage (multifunctionality). In many low density rural territories tourism has been considered as a promising in the framework of diversification of economies, regeneration and development and competitiveness of the territories, supported, increasingly, in sustainability strategies.

This trend reflects the development model implicit in European and national policies, a development paradigm based on a bottom-up perspective, based on the valorisation of heritage and maximisation of endogenous resources for tourism purposes. This implies the involvement and mobilisation of territorial agents (public and private) and communities living in each territory, despite the fact that they are often demotivated and disconnected from the development process.

In this context, in recent years new forms of interaction, cooperation and/or networking have emerged within the public development policies in which the different actors come together to develop shared actions, in a bottom-up perspective, for the construction of a successful sustainable tourism product in a destination area.

The Portuguese Historical Villages Network emerges as a way to enhance the endogenous resources and organize the tourism offer, increasing the competitiveness of the destination, strengthening the collaboration of territorial agents, both intra and inter-territorially, stimulating investment, increasing the technical capacity of the agents and the community, as well as the mobilization of these around a transversal objective as the sustainable development of the tourist destination.

This article is organized in three parts. It starts by discussing the changes that have occurred at the level of development models, public policies, configuring new models of action and governance. Then, the methodological approach adopted to achieve the objectives set out in this work is described. The third part succinctly presents the origins and evolution of the pilot project Historical Villages of Portugal and the main changes in the last community framework, resulting from the application of the main guidelines of public policies for the sustainable development of destinations in low density rural territories.

It concludes with some comments about the main changes operated for the concretization of territorial public policies in the tourist destination under analysis.

2 Literature Review

In recent decades with the social and economic transformations, most rural territories in Europe, particularly the most vulnerable and peripheral ones, have faced, like the western territories, profound processes of reconfiguration, restructuring and even reinvention (Figueiredo 2011; Reis and Baltazar 2019).

The effects of these processes are, naturally, known, to judge by the multiple political debates, approaches in the main official documents and development programmes (European and national) and growing interest of academics in understanding the multiple transformations of “social, economic, political and cultural nature due to the loss of relevance of agricultural activities, but the rebirth of these territories as recreated or reinvented spaces - multifunctional spaces” (Reis and Baltazar 2019, p. 147) is also recognised. According to the authors, rural territories have gained new functionalities and appear associated with new economic activities such as tourism, resulting from new logics of contemporary societies and the growing recognition of the territorial dimension in public policies at the level of the regeneration of these territories through various activities based on the use of territorial assets and, in some cases, untapped ones, for the development of tourism activity (Figueiredo 2018; Reis and Baltazar 2019; Pereira 2018).

In public policies for the development of less favoured rural territories, both in Portugal and in other countries (Correia and Carvalho 2010; Pereira 2018; Silva 2009), tourism has gained particular notoriety as an instrument for the revitalisation of social and economic structures, promoting the recovery of built heritage and the valorisation of endogenous resources, mitigating the loss of human capital and stimulating the dynamization of the local economy. This view is shared by other authors (Kastenholtz, et al. 2014; Reis and Baltazar 2019), who highlight the growing interest in these territories for the development of tourism activity, in which, scale and location are considered structuring and differentiating elements in the construction of new tourism offers (tourism products) and in the affirmation of new tourism destinations in territories traditionally little explored and massified, being the case of tourism networks: Historical Villages of Portugal, the Schist Villages, the Mountain Villages, among others. In these projects, the interventions undertaken sought, based on the new model of development - endogenous and participatory - to adopt new forms of interaction between the different territorial agents, including local communities, in which joined efforts in the dynamization of innovative and sustainable economic activities, based on the existing potentialities with the operationalisation of the action plans of the different development programmes (e.g. PROVERE Programme), as well as in the dynamization, management and competitiveness of some of these tourism networks.

In this context, it becomes evident a growing concern of the different territorial public and private agents (European, national, regional and local) and academics, to combine the new uses of the territories in a multifunctional way and in a balanced and sustainable way, in articulation with the priorities and goals of the Regional Strategy of the Centre, Europe Strategy 2020 and Sustainable Development Goals 2030.

Despite its relevance and global dimension, tourism as an economic and social phenomenon of reference in the contemporary world has, in recent decades, generated some controversy around the “idea that tourism can lead to the destruction of tourism itself” (Brito e Silva 2005, p. 12) due to its universal dimension and characteristics of a sector whose raw materials, in addition to being finite, are, in some cases, non-renewable. The uncontrolled growth of tourism activity, the unbridled consumption of resources, the sharp increase in the number of tourists and tourism consumption, among other factors,

have led to awareness and the need to rethink tourism development in a balanced, sustainable manner and in harmony with territorial resources, thus preventing tourism itself from destroying the foundations of its existence (Brito e Silva 2005) and/or becoming a victim of its own success if it is not guided by principles of sustainability.

This awareness has thus reinforced the importance of sustainability and planning of tourism activity on the agenda of the main policies and programmes that advocate territorial development, so as not to compromise biodiversity, natural and cultural resources, and the well-being of local communities (Correia and Carvalho 2010; Reis 2017), in a medium and long-term perspective.

In this sense, the development of tourism activity should correspond to the principles of sustainability recommended in the Brundtland Report, also known as “Our Common Future” of the World Commission on Environment and Development which introduced a new perspective of integrated development that “meets the needs of current generations without compromising the satisfaction of the needs of future generations” (WCED 1987). In fact, it was from this more universal concept of sustainable development, the principles of the report of the World Commission on Environment and Development (WCED 1987) and other contributions that the World Tourism Organization (WTO 1993; Correia and Carvalho 2010), defined sustainable tourism as a responsible practice, which aims to meet the present needs of tourist consumers (tourist demand) and the receiving regions (tourist destinations), reconciling the development of tourism resources (in the design of tourism supply) with the safeguarding them (for future generations), and increasing the quality of life of local communities with an equitable distribution of economic and social benefits of resource potential without compromising the quality of life of residents and the experience of the visitor himself.

For this reason, tourism development must be done in a way that ensures environmental quality and respects the specificities of each territory, as is the case of the Collective Efficiency Strategies of the Historic Villages of Portugal (EEC AHP), which enshrines the principles of sustainability for the construction of an inclusive, sustainable and intelligent destination with the participation of tourism agents and local community.

3 Objectives, Methodology and Techniques

The present work has as central objectives: to contribute to the theoretical and scientific deepening on public policies, namely on the dialectical relationship they have with the affirmation of “new models of sustainable development” of tourist destinations in low density territories; to identify and analyse the changes that are occurring in the tourist destination Historical Villages of Portugal, arising from the effects of application of public policy guidelines; and to know the dynamics and role of territorial agents in the process of sustainable tourism development.

To carry out this work, we used the traditional qualitative research techniques (Quivy and Champenhoudt 2013), documentary and non-documentary techniques. We sought to conduct a literature review, grounded in exploratory readings on public policies and sustainable development, exposing their interconnections, as well as analyzing the main public policy documents: Action Programme, AHP Benchmark and Evaluation Report of the Strategy of the Historic Villages of Portugal.

Another of the techniques used was the use of participant observation. The distinguishing feature of this data collection technique, in relation to other techniques, consists in the insertion and interaction of the researcher in the observation group, which allows a global and intensive analysis of the object of study (Almeida and Pinto 1990; Itura 2014). As in the other observation methods, the possibility for the researcher to gain, a priori, an in-depth knowledge of the situation and behaviours at the moment they occur in themselves, to the effects they produce in their real social, natural or usual context in which they are observed, stands out.

In this case, participant observation was conducted through conversations and observation of behaviours during the monitoring of activities developed within the EEC AHP, the holding of technical meetings and field visits to the tourist destination. This analysis was reinforced with data obtained from the management entity of the tourist destination, Aldeias Históricas de Portugal - Association for Tourism Development (AHP-ADT), which works directly or more specifically, the general theme exposed here.

4 Empirical Study of the Destination Historical Villages of Portugal

4.1 Network of the Historic Villages of Portugal

The idea of creating the Historic Villages of Portugal Initiative arose in an attempt to intervene in the weakest spaces with structural difficulties, arising from the inability of development models to halt the cycle of territorial abandonment in the interior of the country, reflected in demographic decline and the loss of socio-economic relevance of traditional activities (agriculture and pastoralism), but above all from the adoption of a new alternative development model - the paradigm of endogenous and participatory development - in the late 1980s (Boura 2004; Reis 2017; Reis and Baltazar 2019).

Thus, from the 1980s and early 1990s, a new logic of territorialisation of public development policies was built and affirmed based on assumptions of territorial integration of local and regional development through the valorisation of territorial contexts and endogenous resources, supported by new forms of strategy design, organisation and participation of the multiple actors in the process of territorial development.

This integrated and integrative dimension formed the backdrop for the launch and consolidation of the most emblematic territorial development initiative in the Centre Region (Portugal) - the Programme for the Recovery of Historic Villages -, was implemented under the Rural Development Actions of the Programme Promoting Regional Development Potential (PRDR) of Community Support Framework II (1994–1999), with subsequent continuity in Community Framework III (2000–2006), NSRF (2007–2013) and CSF (2014–2020).

According to Boura (2004), the Historical Villages of Portugal ended up representing the “regional and local incidence of a national strategy, which aimed to discriminate positively some of the spaces landlocked in the Interior of the Centre Region, already considered when the [first] National Tourism Plan was drawn up (1985–1988)” (Boura: 2004, p.117).

The intervention strategy adopted and implemented privileged, then, “the valorization of the patrimonial resources as diversified as the landscape, the places, the built heritage and the referential of cultures, traditional and activities” (Boura 2004, p. 116)

of a set of villages with touristic interest (Almeida, Belmonte, Castelo Mendo, Castelo Novo, Castelo Rodrigo, Idanha-a-Velha, Linhares da Beira, Marialva, Monsanto, Piódão, Sortelha and Trancoso), with a view to retaining the population, attracting tourism and stimulating income diversification through the development of complementary economic activities to the traditional ones, such as the reactivation of traditional arts and crafts in decline (Boura 2004).

On the other hand, the Network of Historic Villages as a mobilising initiative was supported by the Ministry of Planning, Tourism and Culture, as well as the IPPAR, CCRC, local authorities and Inatel.

A mobilisation oriented towards the valorisation of places, cultural and natural heritage, traditions and local productive systems as differentiating factors, but also new forms of organisation of the actors, has constituted the innovative basis of territorial development strategies (local and regional) since the beginning of the 1990s.

In the first two intervention frameworks of public policies (1994–2006), the strategy privileged a set of investment actions from a material perspective: improvement of the living conditions of the populations (basic infrastructures), urban rehabilitation and upgrading and enhancement of heritage, tourism facilities and stimulus to entrepreneurship. In the last two programming periods, between 2007 and 2020, the interventions were framed within the Collective Efficiency Strategy PROVERE - Programme for the Economic Enhancement of Endogenous Resources, taking on a sectorial perspective and centred on the application of support for business activity and attractiveness of the target territory (settlement and renewal of people) and the initiatives of animation, promotion and dissemination of the natural and cultural heritage with strong incorporation of knowledge, in a clear immaterial aspect.

4.2 Results

According to the Action Plano f the Historical Villages of Portugal under the operationalisation of the EEC PROVERE for the programming period 2016–2020, the managing entity (AHP-ADT) established as a central objective the affirmation of the Network of Historical Villages of Portugal as a territory of sustainable and innovative low density based on the concept of green growth, thus continuing the strategy of the previous programming period to leverage the tourist destination as one of excellence and with inimitable resources (AHP-ADT, 2017).

This objective is anchored to the Sustainable Development Goals 2030, in the areas of the Europe Strategy 2020 - Smart Growth, Sustainable Growth and Inclusive Growth, in the axes of smart specialisation of the Regional Strategy of Central Portugal 2020 (RIS 3): rural innovation - enhancing and boosting the value chains of endogenous resources, both in terms of new functionalities (design or digital marketing), and in terms of the design of new products through new forms of local entrepreneurship, in a perspective of green growth; territorial innovation – sustainable and smart Historic Villages (physical rehabilitation, energy efficiency and sustainable mobility); interconnected with the axis of research, development and innovation of the tourism activity in the AHP (development of new products, improvement of tourist experiences and reduction of the ecological footprint in the territory). In addition, there are three transversal axes that reflect a focus on the mobilization and empowerment of territorial agents (public and private)

in order to ensure a quality, diversified and differentiated tourism offer; on animation, communication and territorial promotion; as well as on the evaluation and monitoring of the activities of the EEC AHP 2020 Action Programme (AHP-ADT, 2017).

In this sense, the approach pursued was based on the operationalization of these guiding axes to increase the competitiveness and social cohesion of the tourism destination through innovation (smart growth) and promotion of the efficient use of resources such as natural and historical heritage, traditional knowledge linked to cultural heritage, among others (sustainable growth) and inclusive practices, aimed at improving the tourism experience, differentiation in the context of low-density tourism destinations and increasing the awareness of the AHP brand in the national and international context through a set of anchor-projects (AHP-ADT, 2017).

In this sense, 5 anchor-projects were established that assume a nuclear character of the strategy (public entities), 58 complementary projects (public entities) and 150 private ones for the operationalisation of the strategy, being only the anchor-projects the target of PROVERE funding. The financing of the intentions of complementary and private projects that lead the networking involved the submission of applications to other community funding programmes. As an example, according to the Action Plan, triennium 2016–2018, the approved investment for complementary projects was 25.6 million and 40.4 million for the private projects (AHP-ADT, 2017).

According to data provided by AHP-ADT, between 2016 and 2021, the largest share of investment focused on communication and marketing actions (2.3 million) to increase AHP brand awareness and develop tools with digital content (national and international market). Next comes the investment allocated to the territorial animation project to promote economic activities and heritage values (1.8 million). The third project with the highest investment was the dynamisation, coordination, monitoring and management of the partnership (1.1 million) - governance model - to increase competitiveness and territorial cohesion. It is precisely in this direction that the project of innovation in the design of new products in the tourism sector and adjacent sectors is oriented, with an investment of 472 thousand euros. In addition to this investment, the creation of permanent animation structures for the qualification of the tourism offer (238 thousand euros).

In the second stage of the implementation of the EEC PROVERE, triennium 2019–2021, the creation of the experimentation project - knowledge villages new ways to enhance the existing knowledge in the villages (local, traditional and know-how), using different instruments for its promotion and preservation, in an interaction between residents and visitors or external entities in the development of new innovation processes (114 thousand euros approved) stands out.

In this sense, and considering the guidelines of the main strategic instruments on an international, European, national and regional scale for sustainable development of the territories, the Historical Villages of Portugal - Association for Tourism Development, the entity responsible for managing the network and brand, assumed in the Action Programme under EEC AHP 2020, a set of initiatives organised by the 5 anchor-projects, using tourism as a catalyst for economic, environmental, social and cultural sustainability, through the enhancement of endogenous resources of the Historical Villages of Portugal and stimulating local entrepreneurship. The following table systematises the

main areas of action by anchor-project and some of the results achieved in the period under review: Table 1

Table 1. Key areas of action and results of flagship projects, 2016–2021

Anchor-projects	Areas of action	Results
Communication and Marketing	<ul style="list-style-type: none"> -Identity AHP - Brand AHP -Integrated communication (internal and external) 	<ul style="list-style-type: none"> - Increased AHP brand awareness; - Networked tourist destination with the highest number of followers on social networks; - Increased demand from national and international opinion makers (cinema, television, photographers, writers, etc.); - Participation in fairs, congresses/seminars, etc.; - Growing interest from the media (Portugal and Spain) and specialised media in Europe, USA and Brazil (cycling and walking and sustainability); - Implementation of road signage and completion of the Historical Trails network; - Uniformization of the AHP layout at reception points; - Performance of promotional activities (“<i>De Corpo e Alma</i>”- Best tourism film in the world 2021);
Animation	<ul style="list-style-type: none"> -Territorial animation -Networking -Community 	<ul style="list-style-type: none"> - Setting up a regular entertainment calendar; - AHP-ADT Events: “12 em Rede” – Festive Villages); “The Castles Quest” - Great AHP Route (GR22); - “Ser AHP” - From Concept to Action: Defining Basic Requirements for the Enhancement of the 12 AHP;

(continued)

Table 1. (continued)

Anchor-projects	Areas of action	Results
Innovation	<ul style="list-style-type: none"> - Territorial innovation - Integrated Tourism Products 	<ul style="list-style-type: none"> - AHP Network - 1st sustainable destination in Portugal and 1st in the world in a network (Biosphere Destination seal); - AHP Great Route (the biggest European route to receive the Leading Quality Trails - Best of Europe seal); - Implementation of a monitoring system for the AHP Great Route and Small Routes; - Promotion of cross-selling between regions (Douro/AHP; Tejo/AHP; Serra da Estrela/AHP), according to RIS3;
Permanent Animation Structures	<ul style="list-style-type: none"> - Qualifications 	<ul style="list-style-type: none"> - Upgrading and modernisation of the AHP reception points; - AHP signposting (Walking trails and cultural routes);
Dynamization, Coordination and Follow-up	<ul style="list-style-type: none"> - Fostering common objectives - Strengthening networks 	<ul style="list-style-type: none"> - Actions to make the partnership/consortium more dynamic (meetings of the management bodies; seminars, colloquia and conferences held in the areas in which PROVERE operates; interactions with private consortium members to implement business projects

At the same time, other structuring projects were developed and implemented for the creation of the AHP ecosystem: Historical Villages of Portugal | A More Intelligent Destination and Historical Villages of Portugal | “One more destination #Bikelife”. The former geared towards providing the first destination, networked, fully covered by fibre optics and free wi-fi, aimed at improving the quality of life of residents, tourists and professionals in the tourism sector (intelligent destination). The largest network of cycling routes on road (3.500 kms) was also created, stimulating soft and sustainable mobility practices.

This innovative organisational, procedural, product and service approach imposed greater participation and collaborative work among stakeholders in the development

of sustainable and innovative projects, for affirmation and consolidation as a tourist destination of excellence (University of Aveiro 2019: p.12).

5 Final Reflections

Development models have had substantial changes in recent decades. As a result of these changes, the design and development of public policies have also undergone drastic changes, with territories, including rural territories, being valued as spaces with natural features, with heritage and with relationships (at community level, but also with other territories) capable of promoting and boosting development. These changes bring new hope to territories whose main economic activities were in devaluation and decline.

Tourism is the new opportunity for low density territories, especially by the relationship it makes possible with other sectors, allowing an articulation and interaction between what is constituted as the knowledge of the communities, but, simultaneously, incorporating new activities and new knowledge.

From the analysis undertaken on the object of study it can be observed that the strategy designed for the destination reveals the incorporation of values and standards of endogenous and sustainable development models and the so-called new public policies. It is in this context that is manifested the adoption and application of a new governance model, embodied in an innovative approach at organizational, procedural, product and service levels. This approach was based on cooperative relationships between territorial actors with a view to developing sustainable and innovative projects.

References

1. Almeida, J.F., Pinto, J.: *A investigação nas ciências sociais*. 4ª Ed. Editorial Presença, Lisboa (1990)
2. Boura, I.: Património e mobilização das comunidades locais: Das Aldeias Históricas de Portugal aos contratos de Aldeia. *Cadernos de Geografia* **21**(22), 115–126 (2004)
3. Brito, M., Silva, C.: Turismo e Planeamento: A continuidade ou a auto-destruição. *Revista Turismo Desenvolvimento* **II**(2), 11–24 (2005)
4. Correia, J., Carvalho, P.: Turismo e desenvolvimento rural. O caso do Piódão (Aldeias Históricas de Portugal). *Cadernos de Geografia*, 28/29, 117–130 (2010)
5. Correia, J., Carvalho, P.: Turismo e sustentabilidade do desenvolvimento no contexto das Aldeias Históricas de Portugal. O exemplo do Piódão (Serra do Açor). In: *Atas do 16º Congresso da APDR 2010*, pp. 290–318. APDR, Funchal (2010)
6. Figueiredo, E.: Entre o abandono e o idílico – Representações sociais dos territórios rurais em Portugal. *CULTIVAR – Cadernos de Análise e Prospetiva* **11**, 39–48 (2018)
7. Figueiredo, E.: Um rural cheio de futuros? In: Figueiredo, E. et al. (eds.) *O rural plural – olhar o presente, imaginar o futuro*, pp.13–46. 100 Luz, Castro Verde (2011)
8. Iturra, R.: Trabalho de campo e observação participante em antropologia. In: Silva, A.S., (eds.) *Metodologias das ciências sociais*, pp.149–163. Edições Afrontamento, Lisboa (2014)
9. Kastenholz, E., Eusébio, C., Figueiredo, E., Carneiro, M. e Lima, P.: *Reinventar o turismo rural em Portugal – Cocriação de experiências turísticas sustentáveis*. UA Editora, Aveiro (2014)
10. Pereiro, X.: *Abordagem exploratória do turismo rural de Trás-os-Montes e Alto Douro (Portugal)*. *Análise Social LII* **I**(1), 2182–2999 (2018)

11. Quivy, R., Campenhoudt, L. V.: Manual de investigação em ciências sociais. 6ª Ed. Gradiva, Lisboa (2013)
12. Reis, P., Baltazar, S.: Os territórios rurais de baixa densidade como espaço de lazer e de turismo. O destino turístico Aldeias Históricas de Portugal. *Sociologia On line*, 21, 141–166 (2019)
13. Reis, P.: Turismo, planeamento e desenvolvimento regional – Estratégias de intervenção para a Rede das Aldeias Históricas de Portugal. Universidade de Coimbra, Coimbra (2017)
14. Silva, L.: Casas no campo. Etnografia do turismo rural em Portugal. Imprensa de Ciências Sociais, Lisboa (2009)
15. de Aveiro, U.: Estudo de avaliação da concretização dos Programas de Ação dos PROVERE da Região Centro (2016–2018). Universidade de Aveiro, Aveiro (2019)
16. WCED: O Nosso Futuro Comum. Comissão Mundial do Ambiente e Desenvolvimento, Meriberia, Lider Editores, Lisboa (1987)
17. WTO: Sustainable Tourism Development: Guide for Local Planners. World Tourism Organization, Madrid (1993)



A Review on Gaseous Fuels for Dual-Fuel Diesel Engines

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Abstract. Dual-fuel diesel engines are praised for both being a more environmentally friendly alternative to conventional diesel engines and aiding in a smoother transition from fossil fuels to renewable sources. Depending on the type of dual-fuel engine, they can even be made by modifying an already existing diesel engine. The advantage of dual-fuel diesel engines, besides their ability to use diesel fuel in the case there's no gaseous fuel available, is their versatility regarding the gaseous fuels it can use. The most popular one currently is natural gas, although hydrogen-containing fuels such as biogas, ammonia, and syngas are also being explored as clean and renewable alternatives. Despite their praise, dual fuel engines have yet to be further studied to reduce some of their emissions, such as nitrogen oxides, unburned hydrocarbons, carbon monoxide, and particulate emissions, while at the same time maintaining higher levels of efficiency.

Keywords: Dual-fuel · Diesel engines · Renewable energy

1 Introduction

The state of our planet as we know it in present times is a result of humanity's careless actions, especially since the beginning of the Industrial Revolution. Because of our careless actions as a species, the prognosis of the Earth's future (and in direct consequence, ours too), actions in the form of stricter regulations and initiatives for alternative sources have been taken by most governments – at a greater or lesser extent – to reduce harmful emissions across sectors. The best solution to the ongoing climate change issue – one which most governments agree with – is renewable energy. Contrary to fossil fuels, these sources of energy never run out – like in the cases of solar energy and the kinetic energy of the wind and the ocean – or can be quickly regenerated, like in the case of biomass and energy crops. However, as all previously mentioned before, our huge reliance on fossil fuels doesn't necessarily make this transition an easy feat, and it's very difficult to achieve this on the short run. Moreover, given our reliance on fossil fuels, it's not at all recommendable: such a drastic transition from fossil fuels to renewable sources would truthfully bring upon modern civilization an economic and, ironically, an environmental catastrophe [1]. Before fully transitioning to a new technology, it must be ensured

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that this technology is sufficiently advanced to be replicated at an industrial level, and accessible enough pricewise.

When diesel engines came to existence in the second half of the 19th century, they revolutionized a wide array of industries across the world: they were much more efficient than steam engines and helped companies save huge sums of money since this meant that diesel fuel was much more energy efficient and dense compared to steam [2]. Nowadays, diesel engines are still very much relevant in our daily lives and are used in all sorts of applications, ranging from lawnmowers to motorcycles, and even to push cargo ships across the oceans. Besides transportation applications, diesel engines can also be used for electricity generation in off-grid locations such as small towns or remote islands [3]. Despite their wide array of applications and versatility, diesel engines are very much demonized by the public, because of “Dieselgate”: a result of tampered TDI diesel engines that were sent directly for laboratorial control to make it seem like the engines met US standards when they emitted 40 times more nitrogen oxides than those detected in laboratorial conditions [4]. Since then, there have been stricter regulations regarding diesel engine manufacturing. Despite what the public might still think, diesel engines can play an important role in the transition from fossil fuels to alternate sources. Given the antiquity of this technology, diesel engines have had their efficiency improved upon countless times over its history, and improvements and explorations are still taking place: parameters such as an engines geometry are being explored and studied to help it increase its combustion efficiency – resulting in less fuel being consumed and consequently, less emissions. Treating exhaust emissions through the engine’s tailpipe with the use of catalytic converters or diesel filters is another alternative. A third widely explored alternative is the use of alternative methods such as natural gas, hydrogen, biodiesel, fuel cells, ethanol, among others [5]. This paper’s objective is to look at the different gaseous fuels and their advantages and disadvantages, alongside their emissions and different treatment methods that are available for them.

2 Dual-Fuel Diesel Engines

Dual-fuel (DF) diesel engines are often mixed up with other engine models that have similar yet different principles, such as “bi-fuel” and gas-diesel engines. The former uses two different fuels alternatively while it’s ignited by an external source, whereas the latter employ different methods of introducing gaseous fuel, and don’t undergo auto ignition by themselves [3]. In simple terms, dual-fuel engines use a combination of the compression ignition (CI) and spark ignition (SI) combustion processes [6]. Instead, a small amount of pilot fuel, usually diesel fuel, must be used to trigger an ignition within the engine.

While DF diesel engines can be used with a wide array of gaseous fuels, the primary choice tends to be natural gas (NG). In DF diesel engines NG is a favorite go-to gas to use alongside diesel and this can be seen in the numerous studies that use NG alongside diesel fuel [7]. While other gases can be used in DF mode, NG has several attractive properties which include an energetic content higher than that of gasoline and diesel, a clean nature of combustion – nitrogen oxide (NO_x) emissions are greatly reduced when NG is added, and 20–30% less carbon dioxide is generated, alongside less particulate

matter [7, 8] – and large proven reserves that are more evenly distributed compared to petroleum [8, 9]. These reserves are often located in the same place as petroleum reserves, but they can also be found in dry form or spaces not associated with oil gas fields, and it's possible to find significant NG reserves in more politically stable regions [10].

Because of the wide availability of information, NG is often used as a “standard”: when other gaseous fuels are being combusted, they're oftentimes compared side-by-side with NG to determine their efficiency. An example is this study by Aytav et al., where a NG/mixture is compared to a biogas/diesel mixture in DF mode [11].

3 Alternative Fuels

Despite NG's favoritism, many researchers are studying the properties and potentials of other alternate fuels from renewable sources. The main purpose of alternative fuels is to reduce our dependency from fossil fuels and preferably to encourage the usage of local resources to rely less on outside sources, all while reducing our carbon footprints. Gas energy, like liquid fuel, can be produced from energy crops, but can also be produced from municipal waste, non-food crops biomass, and even water and industrial wastes. Some of the most researched gaseous fuels include biogas, hydrogen, ammonia, and syngas.

3.1 Biogas

One of the main reasons for NG's attractive properties is tied to its methane content. NG is typically composed of around 90% methane, with trace amounts of heavier hydrocarbons (HC) like ethane, propane, butane, and diluent gases like nitrogen and carbon dioxide. Compared to other hydrocarbons – and even compared to gasoline and diesel fuel – methane has a very high lower heating value (LHV) of 50,01 MJ/kg, and its boiling point is drastically lower than that of other HC. Methane is also the responsible one for making NG have a cleaner nature of combustion: NG generally produces between 20–30% less carbon dioxide, 50–87% less HC than methane, and can reduce carbon monoxide emissions up to 95% [9].

It's possible to produce methane in a renewable fashion – this process is known as biogas. This can be objectively achieved by collecting and treating methane from landfills and biomass decomposition, and consequently won't affect food production unlike other biofuels. In a study done by Aytav et al., a conventional DF engine was used to measure and compare the effectiveness of natural gas and biogas, where parameters such as engine vibration, emissions, and engine performance were measured [11]. Diesel fuel with no added gaseous fuel was also tested using the same engine for comparison purposes. In the case of engine vibrations, biogas has shown to lower the amplitude of these vibrations. It's hypothesized that the biogas's high CO₂ and CH₄ content is the cause since CO₂ doesn't react during the combustion phase and reduces the volumetric efficiency of air to fuel (A/F) mixture in the combustion chamber. In the case of CH₄, high concentrations of the gas increase antiknock properties. Regarding performance, the engine on DF mode using biogas/diesel (BG/diesel) mixture has shown a lower thermal efficiency in

all loads, compared to NG/diesel, and diesel alone. Additionally, the BG/diesel mixture showed a higher specific energy consumption than that of NG/diesel and diesel alone. Just like the other two fuels, the specific energy consumption became gradually smaller the higher the loads, illustrating the engine's increased efficiency at higher loads because of the more efficient operating conditions being reached. Lastly, out of all three fuels, BG/diesel had the highest fuel equivalence ratio at all loads. An excessively large means a larger amount of air present which improves conditions for oxidation reactions to take place and may enhance the production of emissions such as NO_x and CO₂, while CO and hydrogen percentages decrease. The larger the fuel equivalence ratio number, more incomplete combustions will take place.

3.2 Hydrogen

Hydrogen is one of the most promising and researched fuels, because of its redeeming qualities, its high energetic content, and its clean production: hydrogen can be made from a wide array of fuels like fossil fuels, biomass, water, and even some industrial chemical waste [12]. However, many of hydrogen's redeeming characteristics also contribute to its instability, such as its high flame speed, wider flammability, and faster burning speeds. This higher instability is not ideal for IC engines since this can lead to a higher incidence of knocking. To not let this gas' potential go to waste – and because our current technology does not allow it – hydrogen is mostly used as an additive for other gaseous fuels, which will be discussed further ahead. There have been, nevertheless, advancements in the development of hydrogen-fueled internal combustion engines over the last two decades, but the same issues that hinder hydrogen's commercialization persist: storage, portability, transport, and purity of the fuel. This has led to exploring other hydrogen-rich fuels such as brown gas, oxyhydrogen, and especially ammonia [13].

3.3 Ammonia

Ammonia has been proposed as an alternative fuel given its hydrogen content and how easy it is to store and transport. Additionally, this carbon-free fuel is lighter than air and is highly soluble in water, which diminishes the risks of any fires or explosions since this property ensure the control of any spillage. Ammonia's high-octane content (<111) equates to less knocking and is an attractive choice for engines with high compression ratios. Ammonia as a single combustion fuel is more plausible, having been studied in the past. However parameters such as its narrow flammability limit, high minimum ignition energy, and high auto-ignition temperatures still complicate its single usage [12, 13]. Even though using ammonia as a single fuel is not quite yet feasible, adding a secondary fuel (such as diesel, kerosene, methanol, ethanol, or gases such as hydrogen and methane) in DF mode can be very beneficial since this secondary fuel can enhance ammonia's properties.

Despite its advantages, ammonia also presents some technical challenges of its own: ammonia is a very difficult fuel to burn given its high latent heat of vaporization (1369.5 kJ/kg, compared to 350 kJ/kg for gasoline and 230 kJ/kg for diesel). It's initially presented in liquid form, and before it burns it must first vaporize and mix

with air. Ammonia is also less dense than gasoline or diesel with a density of only 0,63 kg/liter, and it also has a relatively low energy density per liter: ammonia's LHV is of around 18,8 MJ/kg. For comparison purposes, gasoline's LHV is between 42,5 and 43,5 MJ/kg, and diesel's LHV is between 42,6 and 44 MJ/kg. Some of these challenges can be theoretically alleviated if certain measures are taken: blending ammonia with traditional fuels such as diesel can help lower the ignition temperature and helps reduce the requirements for engine modifications. Not only that but adding traditional fuels – alongside other methods like preheating and higher compression ratios – help reduce flame velocity. More studies should be done to determine the optimum amount of premixed and diffusion combustion and the diesel substitution of the total fuel energy [13]. Another challenging characteristic ammonia has is related to its nitrogen content. Ammonia's evidently high nitrogen content inevitably leads to high NO_x content and unburned ammonia gas when partial combustion takes place. Even though a partial combustion is not ideal, the presence of ammonia combined with the exhaust steam could be beneficial for selective catalytic reduction systems that could subsequently help reduce the NO_x into N_2 .

3.4 Syngas

Also known as synthetic gas or producer gas, syngas is the resulting byproduct of gasification. Despite using mostly coal and other materials with significant CO_2 emissions, what makes gasification such an attractive technology is its versatility: any material can be used so long as there's carbon molecules in its composition [17].

Syngas is composed of methane, carbon monoxide, hydrogen, and small amounts of heavier hydrocarbons, making it considered as a “transition between carbon-based fuels and hydrogen-based fuels”. These fractions can be each larger or smaller depending on factors like raw material, gasifier type, the heat exchange process, and its operating conditions [16, 17]. Syngas composition can change ever so slightly from one process to the next, just like its heating value. For example, if water vapor or oxygen were used as a gasifying agent, the produced syngas would have a heating value between 10–28 MJ/Nm³, whereas the use of air would result in a lower heating value: 4–7 MJ/Nm³. Despite this, a syngas's heating value is not as important as it seems, because in stoichiometric scenarios its energetic density is nearly the same to that of fossil fuels. This is due to its low air-fuel ratio between the syngas and air mixture.

Some characteristics that differentiate syngas from fossil fuels include its high flame propagation speed and its wide flammability limits. Defined as the propagation rate of the normal flame front relative to the unburned mixture, laminar flame speed is an important property for a premixed flame as it gives fundamental information on characteristics such as diffusivity, reactivity, and the exothermicity of the combustible hydrocarbon mixture. [18]. In practice, its flame propagation speed is a characteristic that significantly impacts a motor's efficiency and is calculated based on the ratio of hydrogen and carbon monoxide that's presented in the syngas. Out of all the gases present in syngas, hydrogen demonstrates to have a more significant impact in the flame propagation speed: the more hydrogen present, the faster its speed. A more significant presence of methane is equal to a slower flame propagation speed [19].

Its second characteristic is its wide flammability limits. Also known as explosive range, it can be defined as the limiting values of chemical composition or pressures beyond which ignition cannot be achieved and is bounded by the upper and lower flammability limits (UFL and LFL) which are respectively the maximum and minimum concentrations of fuel in fuel-air mixture that would still allow for ignition-initiated flame to propagate and sustain itself. The presence of this helps the motor use syngas even when it's not in stoichiometric conditions. This parameter is influenced by the composition of the gaseous fuel - particularly by the presence of hydrogen in it - the direction of propagation, size and shape of the combustion chamber, temperature, and pressure [20]. Compared to gasoline and natural gas, syngas is more flammable [19].

Syngas's flammable properties make it an ideal fuel for boilers and DF diesel engines, suggesting that it could even be used as a primary fuel. In a study done by Jatinderpal Singh et al. [21], two syngases from different raw materials were used in DF mode. Although syngas derived from raw cotton stalks outperformed syngas derived from wheat straw, both overall showed significant NO_x emissions decrease yet have also shown increases in HC and CO emissions. This is possibly due to the large amounts of hydrogen and CO present in syngas, alongside being a result of the incomplete combustion that takes place in gasification since this process uses little oxygen.

4 Emissions

Emissions from DF diesel engines are mostly made of diverse NO_x, carbon monoxide, carbon dioxide, hydrocarbons, and particulates. The composition of emissions is influenced by several factors such as fuel composition and properties, the pilot fuel employed, the engine type, size, and geometry, among others. Although NG has a clean nature of combustion and can significantly reduce emissions by up to 95% (for example, with carbon monoxide) and produce nearly no particulate matter and smoke, the same cannot be said for other fuels. Their polluting properties can be reduced or even "taken advantage of" with the help of additives or exhaust gas recirculation (EGR).

4.1 Additives

The purpose of additives is to enhance the properties of the gaseous fuels, ideally to have a higher energy efficiency and to reduce pollutants. The most popular additives used in DF diesel engines are oxygen and hydrogen. Current technologies do not allow us to use these gases as single fuels, so using them as additives is ideal to not let their properties go to waste.

Oxygen. Oxygen has proven to be very beneficial during the combustion process and for reducing certain emissions. Unlike some additives, oxygen is beneficial in both low and high loads: In lower loads, oxygen improves the stability of combustion, accelerates partial oxidation, and a more complete combustion process takes place. In higher load conditions, oxygen decreases ignition delay and shortens combustion durations, leading to a lower tendency to knock. This is especially useful with NG-diesel dual-fuel engines since at high loads too much NG can lead to prolonged ignition delay, allowing time

to transfer heat to the end gas resulting in potential knocking. Oxygen counteracts this. Oxygen enrichment is also a viable technique for DF biogas-diesel engines a high loads due to improvements in several characteristics like thermal efficiency, decreases in the ignition delay, high burning rates, and lower methane emissions [14]. Oxygen also helps reducing CO and HC emissions, and it has been shown to reduce substantially soot emissions and diesel pilot smoke levels. However, it also increases NO_x emissions. This is due to the increase in temperature that takes places during a more efficient combustion process. Another challenge that presents itself is the uncertainty regarding the optimum ratio of oxygen that must be added to the mixture: in high loads, for example, too much oxygen can have the opposite desired effect and encourage knocking [10]. More studies must be done regarding the use of oxygen as an additive to eradicate these uncertainties.

Hydrogen as an Additive. Despite hydrogen being a promising fuel because of its clean and easy production and its qualities which include its fast combustion rate, wide flammability limit, and short quenching distance [15], its instability still makes it unsuitable for its usage as a single fuel. To not waste hydrogen's properties and benefits, researchers have compromised with the prospect of using hydrogen as an additive while more research is done for its use as fuel. As an additive to natural gas, hydrogen has several benefits such as enhancing the gaseous fuel's ignition, increasing its flame velocity, better combustion efficiency, and a more stable combustion. The last characteristic applies in the presence of methane, so this is true for both natural gas and methane when used alone as a fuel. As a result the mixture of natural gas and hydrogen have a lower C/H ratio and therefore emit fewer emissions compared to fossil fuels [16].

Besides the properties mentioned prior, there are several characteristics that make hydrogen more appealing than other fuels and explain why it's such a good additive. Compared to diesel and NG, hydrogen has a higher-octane number of approximately 130, and a high Lower Heating Value (LHV) content of 119, 93 MJ/kg, higher than that of NG and diesel. This means an increased engine efficiency and control of the auto-ignition point, in the case of HCCI engines [17]. Hydrogen's flammability limits are much wider than those of natural gas, and its flammable mixtures can go from an air-to-fuel ratio of as lean as 10 and as rich as 0, 14. Its density is much lower than that of diesel and natural gas, and the same applies to its molecular weight. Additionally, hydrogen's flame velocity is on average nearly ten times faster than that of diesel, and 6, 5 times faster than that of natural gas.

At least since Benbellil et al.'s article [16] publication in November 2021, there has been and there is a lot of publications available about the use of NG enriched with hydrogen used for diesel engines, however the contrary is to be said about articles relating to the use of this same fuel in dual fuel diesel engines. Nevertheless, existing results suggest that adding hydrogen to NG not only improves its brake thermal efficiency, but it also enhances the combustion process by increasing the heat release rate HRR and cylinder peak pressures, and reduces combustion velocity because of hydrogen's higher lower heating value [18, 19].

4.2 Exhaust Gas Recirculation

Exhaust Gas Recirculation (EGR) is an NO_x technique used where part of the emitted NO_x is recirculated back into the combustion chamber with the objective of potentially reburning in the next cycle, and to dilute the oxygen present from the air stream, resulting in a more complete combustion leading to more heat absorption, reducing in-cylinder temperatures and NO_x emissions. Reduction of temperature is essential for less NO_x formations, since NO_x forms in peak temperatures, therefore the decrease in temperature equals to less NO_x formations. Besides NO_x emissions, EGR reduces CO and HC emissions, especially in low to intermediate loads [10, 20]. However, the usage of EGR can be more counterproductive than beneficial in high loads: if large amounts of NG are introduced into the engine, the amount of oxygen available in proportion to the gaseous fuel is subpar and there's not enough oxygen for combustion. This would instead aggravate the problem and create more CO and HC emissions [20].

Despite the amount of research done already regarding this subject, some uncertainties remain yet to be sorted out, such as those related to stationary applications where EGR temperatures could be controlled, and finding an optimum EGR percentage where NO_x reduction in large quantities can still be achieved without having to compromise things such as thermal efficiency [10]. In the case of finding the optimum EGR percentage, this issue arises from the fact that the ratio of optimum EGR percentage changes depending on the operating conditions. High levels of NG involve more air being consumed and used, and EGR becomes unviable even though NO_x levels increase drastically because of the high temperatures that are being worked with. In the case of stationary applications, more studies must be done regarding the ideal amounts of cooled EGR and hot EGR to find the best balance between NO_x reduction and optimal thermal efficiency.

EGR and H₂ as an Additive. EGR may help reduce NO_x emissions, but when levels are too high this can deteriorate the combustion process and increase the levels of other emissions such as CO, HC, and PM. A solution that has been proposed for this issue is adding hydrogen to help stabilize combustion, since it has been widely studied within the use of NG. Hydrogen helps increase the reactivity of the gaseous fuel and counterbalance the slow mixing and combustion rates caused by high EGR amounts, thus making the combustion process more efficient. Additionally, adding hydrogen helps reduce greenhouse gas emissions such as those of CO₂ and CH₄, due to the lowered carbon-to-hydrogen ratio of the blended gaseous fuels and the improved combustion. It has been shown that on average, for every 10% of H₂ concentration increased, HC and CO emissions were reduced by 15–20%, and PM emissions were reduced by 10%. With enough concentrations of hydrogen, black-carbon emissions could be eliminated [10].

Despite all these benefits, there's also a catch: increasing hydrogen concentration also increases NO_x emissions, which could be due to the higher temperatures found within the cylinder, or the increased prompt-NO formation due to increased OH radical concentrations. Overall, more research must be done regarding this topic to find a proper compromise and the optimum ratios and conditions for its best work.

5 Conclusion and Future Direction of Research

DF technology is a promising step in the right direction, and a great technology that aids in the transition from fossil fuels to renewable sources. Like any other technology, DF engines are in a constant process of improvement and exploration. Besides the well-known NG, alternative fuels of cleaner origins such as biogas, hydrogen, ammonia, and syngas are being researched. Most of these fuels have a great potential mostly because of their hydrogen content, and some have the added advantage of being carbon neutral. Despite the wide amount of research available on DF diesel engines, most researchers suggest for future and more comprehensive research to take place. The composition of gaseous fuels is a topic that remains having a lot of research potential. For example, NG has several shortcomings that include limited replacement ration, efficiency deterioration, low combustion efficiency due to the incomplete combustion nature of methane, lower gas energy density compared to that of other HC, and unburned methane emissions, which are an issue because of their high global warming potential. Other fuels present their own issues, like hydrogen and their instability, and ammonia with its high nitrogen content and corrosive properties. The current technology allows for these setbacks to be mitigated with the help of additives as seen before, yet further research is encouraged to develop new technologies compatible with these fuels.

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References

1. Boretti, A.: Advantages and disadvantages of diesel single and dual-fuel engines. *Front. Mech. Eng.* **5**, 1–15 (2019). <https://doi.org/10.3389/fmech.2019.00064>
2. Lemelson-MIT. Rudolf Diesel Internal Combustion Engine.
3. Karim, G.A.: *Dual-Fuel Diesel Engines*, 1st edn. CRC Press Taylor & Francis Group, Boca Raton (2015)
4. EPA. Learn About Volkswagen Violations. [Online]. Available: <https://www.epa.gov/vw/learn-about-volkswagen-violations>
5. Mourad, M., Mahmoud, K.R.M., NourEldeen, E.S.H.: Improving diesel engine performance and emissions characteristics fuelled with biodiesel. *Fuel* **302**, 121097 (2021). <https://doi.org/10.1016/j.fuel.2021.121097>
6. Maurya, R.K., Mishra, P.: Parametric investigation on combustion and emissions characteristics of a dual fuel (natural gas port injection and diesel pilot injection) engine using 0-D SRM and 3D CFD approach. *Fuel* **210**, 900–913 (2017). <https://doi.org/10.1016/j.fuel.2017.09.021>
7. Mohamad, F., Cahyono, B., Abu, R., Birouk, M.: Performance and emissions of natural gas/diesel dual-fuel engine at low load conditions : effect of natural gas split injection strategy. *Fuel* **300**, 121012 (2021). <https://doi.org/10.1016/j.fuel.2021.121012>
8. Guo, H., Li, H., Guzzella, L., Shioji, M.: Editorial: advances in compression ignition natural gas–diesel dual-fuel engines. *Front. Mech. Eng.* **7**, 642187 (2021). <https://doi.org/10.3389/fmech.2021.642187>

9. Lazăr, C., Lazăr, M.: Economic Insights-Trends and Challenges Use of Statistical Indicators to Measure Crude Oil and Natural Gas Reserves and Production.
10. Hegab, A., La Rocca, A., Shayler, P.: Towards keeping diesel fuel supply and demand in balance: dual-fuelling of diesel engines with natural gas. *Renew. Sustain. Energy Rev.* **70**, 666–697 (2017). <https://doi.org/10.1016/j.rser.2016.11.249>
11. Aytav, E., Koçar, G., Teksan, A.E.: Experimental comparison of biogas and natural gas as vibration, emission, and performance in a diesel engine converted to a dual fuel. *SAE Int. J. Fuels Lubr.* **13**(1), 61–78 (2020). <https://doi.org/10.4271/04-13-01-0004>
12. Kurien, C., Mittal, M.: Review on the production and utilization of green ammonia as an alternate fuel in dual-fuel compression ignition engines. *Energy Convers. Manage.* **251**, 114990 (2022). <https://doi.org/10.1016/j.enconman.2021.114990>
13. Boretta, A.: Novel dual fuel diesel-ammonia combustion system in advanced TDI engines. *Int. J. Hydrogen Energy* **42**(10), 7071–7076 (2017). <https://doi.org/10.1016/j.ijhydene.2016.11.208>
14. Cagua, K., Amell, A., Cadavid, F.: Effects of oxygen enriched air on the operation and performance of a diesel-biogas dual fuel engine. *Biomass Bioenerg.* **45**, 159–167 (2012). <https://doi.org/10.1016/j.biombioe.2012.06.003>
15. Li, Y., Zhang, Z., Liu, Z., Tong, P., Yang, D., Zhang, W.: Effect of negative valve overlap on combustion and emissions of CNG-fueled HCCI engine with hydrogen addition. *Int. J. Aerosp. Eng.* **2021**, 1–14 (2021). <https://doi.org/10.1155/2021/8898796>
16. Benbellil, M.A., Lounici, M.S., Loubar, K., Tazerout, M.: Investigation of natural gas enrichment with high hydrogen participation in dual fuel diesel engine. *Energy* **243**, 122746 (2021). <https://doi.org/10.1016/j.energy.2021.122746>
17. Hairuddin, A.A., Yusaf, T., Wandel, A.P.: A review of hydrogen and natural gas addition in diesel HCCI engines. *Renew. Sustain. Energy Rev.* **32**, 739–761 (2014). <https://doi.org/10.1016/j.rser.2014.01.018>
18. Ouchikh, S., Lounici, M.S., Tarabet, L., Loubar, K., Tazerout, M.: Effect of natural gas enrichment with hydrogen on combustion characteristics of a dual fuel diesel engine. *Int. J. Hydrogen Energy* **44**(26), 13974–13987 (2019). <https://doi.org/10.1016/j.ijhydene.2019.03.179>
19. Lounici, M.S., Boussadi, A., Loubar, K., Tazerout, M.: Experimental investigation on NG dual fuel engine improvement by hydrogen enrichment. *Int. J. Hydrogen Energy* **39**(36), 21297–21306 (2014). <https://doi.org/10.1016/j.ijhydene.2014.10.068>
20. Nag, S., Sharma, P., Gupta, A., Dhar, A.: Experimental study of engine performance and emissions for hydrogen diesel dual fuel engine with exhaust gas recirculation. *Int. J. Hydrogen Energy* **44**(23), 12163–12175 (2019). <https://doi.org/10.1016/j.ijhydene.2019.03.120>



An Effective Solution for Reinforcing 3D Concrete Printable Composites

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Abstract. The use of 3D concrete printing, a technology within the scope of Industry 4.0, is rapidly increasing worldwide. Despite its revolutionary advantages for the construction industry, several challenging problems need to be solved. Technical reinforcement is a critical issue. Several solutions have been proposed, though all of them limit the advantages 3D printing can provide. Considering that 3D printing technology allows almost unlimited geometric freedom, it is clear that these complex geometries will be hard to reinforce either with construction reinforcements or meshes. This work aims to overcome this constraint with textile reinforcements, allowing this way to take full potential of this new technology in terms of structural design and architectural shape.

Keywords: 3D printable concrete · Reinforcement · Textile reinforcement

1 Introduction

Digital concrete production is an extremely promising and vivid research topic, enabling the construction industry to build complex structures faster, productively, and cost-effectively with increasing automation. Other advantages include greater geometric freedom, a shorter supply chain, lower energy consumption, less waste, savings in formwork and labour, safer job sites and gender equality through the use of robotic systems, and opportunities for construction workers to learn new skills [1–8].

Digital concrete promises to revolutionize structural design by facilitating creativity. In addition, 3D printing is considered environmentally friendly due to the potential use of recycled raw materials such as construction and industrial waste and the ability of 3D-printed buildings to minimize waste and dust generation compared to traditional methods [9–13].

3D concrete printing is a disruptive innovation technology for the construction industry, though there are some challenges to be solved. Some examples are the 3D printer dimensions, the directional dependence of the produced concrete, and the lack of standards and regulations [14–18].

1.1 Challenges of 3D-Printing Concrete

Conventional concretes are not suitable for use in 3D printers as they do not meet rheological requirements. Several research teams and industrial manufacturers have been trying to optimize the fresh properties of concrete to make it printable, mostly by replacing coarse aggregates by finer ones and pozzolans, such as sand, clay, fly ash and silica fume, have been used for this purpose. However, printable concrete became highly susceptible to cracking, as coarse aggregates are required to control excessive shrinkage. To overcome this problem, fiber reinforcements and shrinkage reduction or compensating admixtures have been tested [13].

There are many studies on 3d printable concretes, though not enough attention has been paid to the materials used for building-scale 3D printing. Several engineering challenges associated with the “printability” of the concrete materials used for building-scale 3D printing have been overcome, though most of these works ignore the inherent weaknesses of conventional concrete and its implications for 3D printed structures (Scheurer et al. 2020; Souza et al. 2020; [9, 12, 13, 19]).

Generally, when it comes to concrete structures, the most important problem is that cementitious materials do not have sufficient tensile capacity and ductility for their intended applications, so steel reinforcement is typically used to carry tension within the concrete. Conversely, 3D printing technologies offer almost unlimited geometric freedom, so this complex geometry need to be reinforced. This reinforcement is not possible with traditional construction reinforcements or meshes, so these new technologies won't be used to their full potential in terms of structural design and architectural forms. Additionally, the moldless structure largely eliminates the external vibration of the 3D printed concrete, weakening the concrete-rebar connection. Thus, it is clear that the reinforcement concepts and principles applied to conventional concrete structures (designed to overcome the tensile limitations of concrete) cannot be applied in 3D printing. [10, 19, 20, 21].

2 Reinforcement Strategies for 3D-Printed Concrete

Despite the 3D printing's many advantages, its application in construction is still limited due to the difficulty of adding reinforcements to achieve needed strength and ductility. Several reinforcement strategies have been proposed in the literature to solve this limitation, as follows:

- Printable fibre reinforced concrete [22]; Portland cement paste and reinforcing short fibres (carbon, glass and basalt fibres, 3–6 mm) are studied. Alignment of the fibres caused by the 3D-printing process is observed, opening up the possibility of using the print path direction to control fiber orientation within the printed structures. A schematic diagram of the fiber alignment and a sample photograph of the aligned reinforcement is illustrated in Fig. 1.

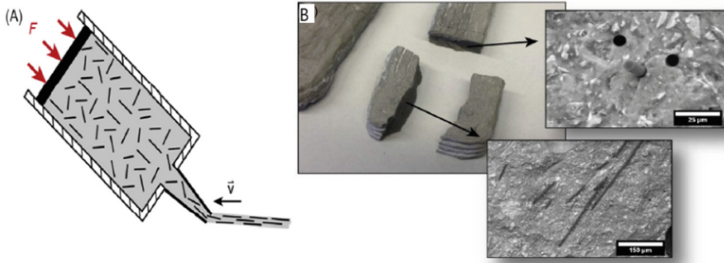


Fig. 1. (A) Schematic diagram of the nozzle-injection technique: by pressing the fiber-reinforced paste through a syringe, fibers are aligned parallel to the movement of the nozzle, (B) Photograph of a sample containing aligned reinforcement fibers and corresponding ESEM micrographs showing the fiber orientation (perpendicular and parallel to the fracture surface of the specimen) [22].

- External reinforcement arrangements: 3D-printing integrated concrete mold and the placing of vertical reinforcement in this mold to be filled with fluid or vibratory concrete, as shown in Fig. 2 [23];



Fig. 2. Application of external reinforcement arrangements [23]

- Adding high-strength steel fibres to the concrete during printing (TU Eindhoven, 2017);
- Concrete printing around fixed steel reinforcement, and concrete and reinforcement printing with multiple arms running in parallel [24].

Although these strategies can address the limitations of 3D-printed concrete structures to some extent, the proposed solutions are not yet satisfactory, particularly regarding an adequate reinforcement of 3D-printed concrete structures with complex geometries (e.x. double curved) remains a challenge [20, 21].

When it comes to 3D-printed concrete, the most adopted strategy, especially for industrial companies, is to use the 3D-printed concrete as a mould to build channels-like structures to contain the rebars. Inside these channels, the steel reinforcements can be positioned vertically for the columns (as shown in Figs. 3a and b) or horizontally (manually or digitally controlled) after the compression of each layer, enhancing the stability of the structure (see Fig. 3c). These channels are then filled with conventional flowable concrete. Similarly, printing concretes at both sides of a steel grid using a modified forked nozzle is a feasible way to combine structures with vertical and horizontal reinforcements (Fig. 3d). A flexible reinforcement wire coil can be placed, providing longitudinal tensile strength and ductility, while concrete is printed using devices connected to the nozzle (see Fig. 3e). This approach has been commercially used by the Chinese company HuaShang Tengda [25].

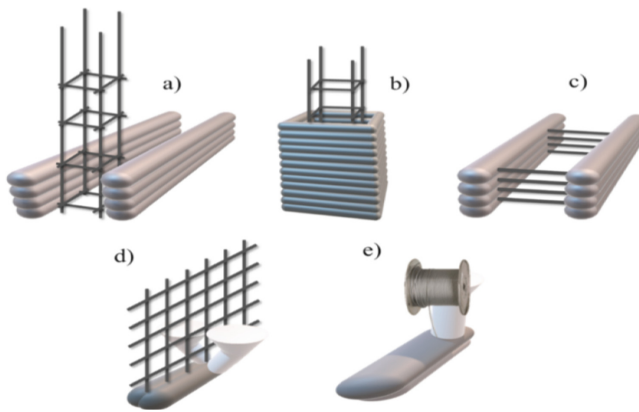


Fig. 3. Designs of structures for printing: a,b) channels with vertically-positioned steel reinforcements; c) channel supported by horizontally-positioned steel reinforcements; d) wall supported by a pre-fabricated steel grid with laying concrete at both sides and e) layers reinforced with a flexible steel cable inserted during printing using a spool-like device.

As noted by Asprone et al. [20], the deterioration of reinforced concrete structures is mainly due to the corrosion of steel reinforcement, there are very few studies on non-metallic reinforcement, for example regarding composite materials. Fibers and continuous fiber-based materials (traditionally referred to as technical textiles) offer some advantages over conventional metal-based materials, as they have highly modifiable mechanical properties, such as strength, elongation, tensile strength, the high strength-to-weight ratio of Young's modulus, and variable porosity) [12].

2.1 Strain Hardening Cementitious Concrete

Recent reinforcement works are focused on Strain Harden Cementitious Concrete (SHCC). Considering the potential provided by fibers, this type of concrete could offer a possible solution for the reinforcement problem. In this approach, printable reinforced

3D concrete is produced using short fibres. SHCC exhibits multiple thin cracks and strain-hardening properties under tensile loading. In addition to its extremely high mechanical performance under static and dynamic loading, SHCC has a number of other advantages: 1) SHCC-specific narrow cracks are suitable for the durability of structural members, 2) The fine polymeric fibers used in SHCC help to reduce the negative consequences of shrinkage (plastic, autogenous and drying) that occur in the absence of coarse aggregate. This way, crack formation can be prevented [9, 13]. This fiber-reinforced 3D printable concrete can meet building-scale steel reinforcement needs, thus providing greater freedom and efficiency [19].

Nevertheless, this method is suitable for low-rise buildings, where load-bearing capacity is not required, and so far the building solutions to be printed have a maximum of five floors. The tensile strength of 3D printed concrete structures must be increased, and new strategies must be found for printing high-rise buildings requiring higher bearing capacity.

As illustrated in Fig. 4, different geometries have been adopted to improve the load-bearing capacity and the stability of walls produced with concrete through the SHCC approach [13]. However, the SHCC approach also significantly limits the freedom of complex architectural designs, which is a crucial benefit of 3D printed concrete technology.

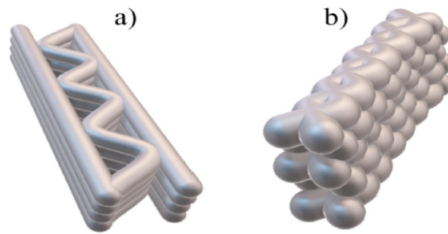


Fig. 4. Examples of 3D printing components with different geometries [13].

The various concepts and prototypes presented are promising, but none of them fully meets the relevant requirements for the wide-ranging application of 3D printed concrete, further progress is needed [9].

According to Nerella et al. [9] and Souza et al. [13], further investigation is required, allowing the use of construction reinforcements with fiber that can bear the tensile strength of structures solving the reinforcement issue. There is an urgent need to create new technology for reinforcing 3D-printed structural components.

On the other hand, Souza et al. [13] point out that new materials can contribute to the solution, emphasizing the inadequacy of existent methods and materials.

3 Using Textile Reinforced Matrix in 3D Printing Method

Textile materials can significantly improve the mechanical behaviour of cement matrices under static and dynamic conditions, providing superior tensile strength, toughness,

ductility, energy absorption and protection against environmental degradation [26]. In recent years, the application of textile reinforced concrete (TRC) in the construction industry has got a lot of attention. Textile reinforced concrete (TRC) is based on the use of inorganic-based matrices, instead of organic-based resin matrices. These textile reinforced concretes are not only used in civil engineering [27, 28], but also are a strong alternative method to reinforcements with FRP composites for reinforcement purposes.

Commonly, cementitious mortar matrices are used, though lime mortar matrices can also be used [29]. FRP reinforcement and fabric materials can be utilized as reinforcement materials. Textile reinforcements are often made from carbon, basalt and glass fibre, which can increase the durability and lightness requirements for concrete structures.

In addition, TRC has high formability compared to steel-reinforced concrete [27, 28], so TRC is particularly competitive for complex thin-shell structural members with fine-grained concrete matrices [21].

The abovementioned advantages of reinforcing textiles have led some research teams to investigate its application in concrete. Research on textile meshes as reinforcements for cementitious products started in the early 1980s and generated a new class of materials – textile reinforced concrete (TRC). Developments progressed rather slowly until the end of the 1990s. But over the last 20 years, remarkable progress has been made on this subject, especially in new structures [30]. Further research on this material is still necessary, though the first commercial applications are available, including precast elements, such as facades, and complex load-bearing structures, such as bridges, as well other applications in strengthening reinforced concrete structures [12, 31].

In the TRC method, a mortar matrix is laid on the surface of the structure to be strengthened, the reinforcement material is then placed on this matrix, and covered with a mortar matrix. Figure 5 shows the TRC system and its implementation.

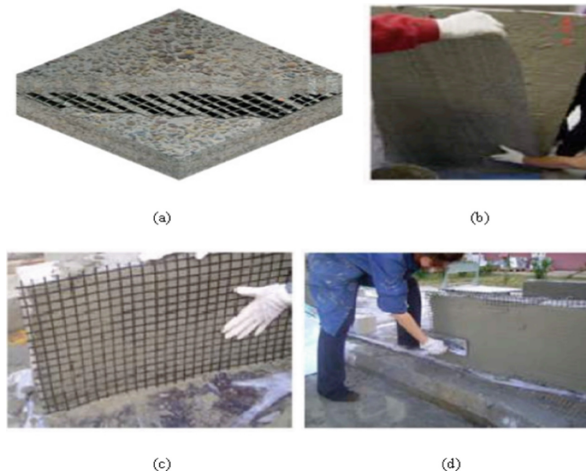


Fig. 5. (a) TRM layered view, (b)(c)(d) installation of TRM to the system, respectively

3.1 Advantages of Using Textile Reinforcement with 3D Printed Concrete

Compared with traditional steel reinforcements, textile reinforcements offer several advantages as these materials are perfectly suited for 3D printing construction, as follows:

- Higher specific strength. These lightweight materials have high strength, so they will not put an extra load on the 3D concrete layers, on top of supporting the transport of the upper layers.
- Good formability; the material can be produced according to the requirements, can be cut and bent. Considering architectural design freedom, this material allows all the needed design freedom for the 3D printing,
- Corrosion resistance; The materials commonly used for TRC do not corrode, so the minimum concrete coverage traditionally required can be greatly reduced (up to 80%), allowing the fabrication of thin-walled elements, which can lead to new architectural possibilities.

Conversely, fine aggregates with a particle size of less than 4 mm are used in the concrete design produced for TRC, in line with the production of 3D printable concrete [12]. In addition, the presence of textile reinforcement does not reduce the fluidity of concrete like the SHCC, so the problem of cold joint formation is minimized, not requiring any measure to prevent it.

3.2 Evaluation of the Use of Textile Reinforcement Within 3D Printed Concrete

Scheurer et al. [12], continuous fibre-based reinforcements (textiles) offer a promising alternative to reinforce 3D printing cement- or lime-based matrices, as textile reinforcements can be tailored to suit various design requirements. It seems suitable textile reinforcement solutions can be selected for different approaches to improving digital concrete production. Figure 6 shows Scheurer et al. [12] proposal to apply fiber reinforcement within 3D-printed concrete.

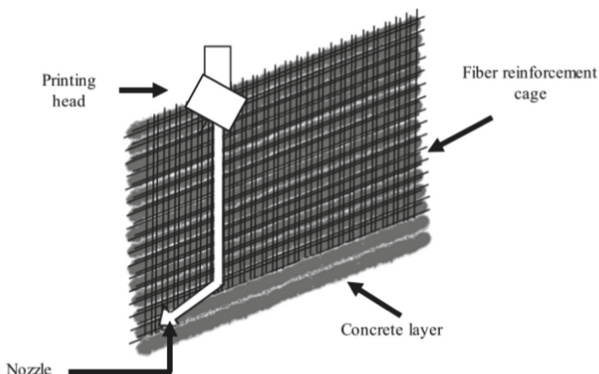


Fig. 6. Proposal of textile reinforcement for 3DP concretes [12]

The most important parameter determining fiber selection on textile production is material selection. The chosen textile material must be a lightweight material with a high strength.

According to the reinforcement evaluation, carbon has good tensile strength and low thermal expansion, but it is expensive, not adhering well to concrete and lime-based matrices. Basalt is formed by melting basalt rock, so it is more cost-effective than carbon and has good tensile strength.

In addition to meeting these criteria, there is a need to pay attention to the casting conditions and rheological properties of the 3D printing material to tolerate the cold joint areas that may occur at the interfaces of the 3D layers. There is also a need to investigate the compatibility between the textile material and the matrix, that is why basalt textile is recommended as a textile reinforcement material as it has a good bond behaviour either with cement or lime matrices due to its natural structure.

4 Conclusions

One of the most important challenges in 3D concrete studies is the reinforcement problem, especially at the structural scale. It is essential to reinforce the buildings to be produced by 3d printing. However, traditional reinforcement techniques are not suitable as they limit the geometric design freedom, a major advantage of 3d printed concretes. This work discusses the reinforcement of 3D printed concrete elements with textile-based reinforcement materials.

Existing 3D concrete studies did not address the advantages of a textile-reinforcement material for 3D concrete structures. Most of them use steel-based reinforcements or short fibres added to the concrete matrix in 3DP concretes. In this work, textile fibres are considered the best reinforcement material, allowing to take full potential of this new 3DP technology in terms of structural design and architectural shape.

References

1. Lim, S., Buswell, R.A., Le, T.T., Austin, S.A., Gibb, A.G., Thorpe, T.: Developments in construction-scale additive manufacturing processes. *Autom. Constr.* **21**, 262–268 (2012)
2. Wolfs, R.: 3D printing of concrete structures. Graduation thesis, Eindhoven University of Technology, Department of the Built Environment Master Architecture, Building and Planning Specialization Structural Design, Netherlands (2015)
3. Wu, P., Wang, J., Wang, X.: A critical review of the use of 3-D printing in the construction industry. *Autom. Constr.* **68**, 21–31 (2016)
4. Labonnote, N., Rønquist, A., Manum, B., Rüter, P.: Additive construction: state-of-the-art, challenges and opportunities. *Autom. Constr.* **72**, 347–366 (2016)
5. Craveiro, F., Bartolo, H.M., Gale, A., Duarte, J.P., Bartolo, P.J.: A design tool for resource-efficient fabrication of 3D-graded structural building components using additive manufacturing. *Autom. Constr.* **82**, 75–83 (2017)
6. Camacho, D.D., et al.: Applications of additive manufacturing in the construction industry—a forward-looking review. *Autom. Constr.* **89**, 110–119 (2018)
7. Maskuriy, R., Selamat, A., Maresova, P., Krejcar, O., David, O.O.: Industry 4.0 for the construction industry: review of management perspective. *Economies* **7**, 68 (2019)

8. Tarhan, Y., Şahin, R.: Fresh and rheological performances of air-entrained 3D printable mortars. *Materials* **14**(9), 2409 (2021)
9. Nerella, V. N., Ogura, H., Mechtcherine, V.: Incorporating reinforcement into digital concrete construction. In: *Proceedings of IASS Annual Symposia* (Vol. 2018, No. 7, pp. 1–8). International Association for Shell and Spatial Structures (IASS) (July 2018)
10. Ogura, H., Nerella, V.N., Mechtcherine, V.: Developing and testing of strain-hardening cement-based composites (SHCC) in the context of 3D-printing. *Materials* **11**(8), 1375 (2018)
11. Tarhan, Y., Şahin, R.: Developments of 3D concrete printing process. In: *International Civil Engineering and Architecture Conference*, Trabzon/Turkey (2019)
12. Scheurer, M., Dittel, G., Gries, T.: Potential for the integration of continuous fiber-based reinforcements in digital concrete production. In: Bos, F.P., Lucas, S.S., Wolfs, R.J.M., Salet, T.A.M. (eds.) *Second RILEM International Conference on Concrete and Digital Fabrication*. RILEM Bookseries, vol. 28, pp. 701–711. Springer, Cham (2020). https://doi.org/10.1007/978-3-030-49916-7_70
13. Souza, M.T., Ferreira, I.M., de Moraes, E.G., Senff, L., de Oliveira, A.P.N.: 3D printed concrete for large-scale buildings: an overview of rheology, printing parameters, chemical admixtures, reinforcements, and economic and environmental prospects. *J. Build. Eng.* **32**, 101833 (2020)
14. Kreiger, M.A., MacAllister, B.A., Wilhoit, J.M., Case, M.P.: The current state of 3D printing for use in construction. In: *Proceedings of the 2015 Conference on Autonomous and Robotic Construction of Infrastructure*, Ames, IA, USA, 2–3 Jun [MT1][RS2] 2015, pp. 149–158 (2015)
15. Bos, F., Wolfs, R., Ahmed, Z., Salet, T.: Additive manufacturing of concrete in construction: potentials and challenges of 3D concrete printing. *Virtual Phys. Prototyping* **11**(3), 209–225 (2016)
16. Panda, B., Tan, M.J.: Experimental study on mix proportion and fresh properties of fly ash based geopolymer for 3D concrete printing. *Ceram. Int.* **44**(9), 10258–10265 (2018)
17. Ingaglio, J., Fox, J., Naito, C.J., Bocchini, P.: Material characteristics of binder jet 3D printed hydrated CSA cement with the addition of fine aggregates. *Constr. Build. Mater.* **206**, 494–503 (2019)
18. Tarhan, Y., Tarhan, İH., Craveiro, F., Bártolo, H.: Sustainable materials for additive manufacturing: earth-based concrete. In: da Costa Sanches Galvão, J.R., et al. (eds.) *Proceedings of the 1st International Conference on Water Energy Food and Sustainability (ICoWEFS 2021)*, pp. 708–716. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-75315-3_75
19. Soltan, D.G., Li, V.C.: A self-reinforced cementitious composite for building-scale 3D printing. *Cement Concr. Compos.* **90**, 1–13 (2018)
20. Asprone, D., Menna, C., Bos, F.P., Salet, T.A., Mata-Falcón, J., Kaufmann, W.: Rethinking reinforcement for digital fabrication with concrete. *Cem. Concr. Res.* **112**, 111–121 (2018)
21. Wang, W., Konstantinidis, N., Austin, S.A., Buswell, R.A., Cavalaro, S., Cecinia, D.: Flexural behaviour of AR-glass textile reinforced 3D printed concrete beams. In: Bos, F.P., Lucas, S.S., Wolfs, R.J.M., Salet, T.A.M. (eds.) *Second RILEM International Conference on Concrete and Digital Fabrication*. RILEM Bookseries, vol. 28, pp. 728–737. Springer, Cham (2020). https://doi.org/10.1007/978-3-030-49916-7_73
22. Hambach, M., Rutzen, M., Volkmer, D.: Properties of 3D-printed fiber-reinforced portland cement paste. In: *3D Concrete Printing Technology*, pp. 73–113. Butterworth-Heinemann (2019)
23. Apis Core Homepage. <https://www.apis-cor.com/workshops>. Accessed Feb 2022
24. Scott, C.: Chinese Construction Company 3D Prints an Entire Two-Story House On-Site in 45 Days. *3dprint.com* (2016). Available: <https://3dprint.com/138664/huashang-tengda-3d-print-house/>. Accessed 20 Mar 2017

25. Mechtcherine, V., Nerella, V.N., Will, F., Näther, M., Otto, J., Krause, M.: Large-scale digital concrete construction—CONPrint3D concept for on-site, monolithic 3D-printing. *Autom. Constr.* **107**, 102933 (2019)
26. Peled, A., Mobasher, B., Bentur, A.: *Textile reinforced concrete*. CRC Press, Boca Raton (2017)
27. Hegger, J., Voss, S.: Investigations on the bearing behaviour and application potential of textile reinforced concrete. *Eng. Struct.* **30**, 2050–2056 (2008). <https://doi.org/10.1016/j.engstruct.2008.01.006>
28. Hawkins, W., Orr, J., Ibell, T., Shepherd, P.: An analytical failure envelope for the design of textile reinforced concrete shells. *Structures* **15**, 56–65 (2018). <https://doi.org/10.1016/j.istruc.2018.06.001>
29. Alecci, V., et al.: Experimental investigation on masonry arches strengthened with PBO-FRCM composite. *Compos. B Eng.* **100**, 228–239 (2016)
30. Papanicolaou, C.G., Triantafillou, T.C., Karlos, K., Papathanasiou, M.: Textile-reinforced mortar (TRM) versus FRP as strengthening material of URM walls: in-plane cyclic loading. *Mater. Struct.* **40**(10), 1081–1097 (2007)
31. Raupach, M., Morales Cruz, C.: Textile-reinforced concrete: selected case studies. In: Triantafillou, T. (ed.) *Textile Fibre Composites in Civil Engineering*, pp. 3–24. Elsevier, Amsterdam (2016)



Reactant or Product?: Fate of Water During HTC Under Different Conditions

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Abstract. This work aims to give insight about this concern by making a systematic study of how temperature (150–250 °C) and time (30–60 min) affect the distribution of fractions during HTC. Both solid (hydrochar) and liquid characterization made by suitable techniques were employed to elucidate reaction pathways and to identify interactions between variables.

By making thoughtful quantification of the solid and liquid phases, and considering the reactions involved on HTC processes, it was possible to elucidate the reaction conditions that favour the formation of water, and those that are more prone to yield a less dense liquid.

Pistachio nut shell was degraded at different extent degrees, from almost an unperceptible degree (150 °C, 30 min) to reach a coal-like aspect, and heating values close to that of lignite (23 MJ/kg, for harshest reaction conditions).

1 Introduction

The shift of the worldwide energetic model towards a greater contribution of renewable sources of energy, less centralized and more efficient, is mandatory. Numerous national and international agreements such as the recent European Green Deal [1], are pushing R&D strategies all over the world in this frame.

Biomass has demonstrated its key role on the way to this next scenery, mostly due to well-known properties such as zero CO₂ net emissions, versatility, abundancy, spread character and because it facilitates the disposal of wastes otherwise toxic to the environment. The methods used to treat biomass, however, defines how green is the whole process, in terms of energy cost, production of potentially toxic by products, etc.

Pistachio nut shell (PNS) was chosen as raw material due to two main reasons: a) it is a very homogeneous material, what makes it very suitable to be used for a rigorous experimental study in which determining the effects of thermodynamical properties on the reaction products is the main target; in addition its hardness makes it ideal to yield granular carbon materials; b) it is a very abundant biomass waste in south west Spain and many Mediterranean areas. The outstanding nutritional properties of this fruit make this material be named as green gold, and the market has experienced a buoyant growth; last reports (dating may 2022) forecast a continuous rising tendency on next years [2].

Previous pieces of research have successfully probed the suitability of PNS as precursor for carbon materials manufacture. For example, Xu et al. (2018) [3] investigated the suitability of PNS as anode materials in Na ion batteries; Hassan et al. (2015) [4] have used PNS to prepare activated carbons that could be used as adsorbents for pesticides in water. We, in a previous paper (2018), investigated the use of porous PNS HCs to remove some emerging microcontaminants (caffeine) from liquid solutions.

Hydrothermal carbonization (HTC) of biomass is one of the several thermochemical methods that can be used today to upgrade biomass and convert it into high value products. HTC consists on the degradation of biomass in the presence of water under subcritical conditions and autogenous pressure [5]. Under temperatures as low as 180–260 °C and only using for several hours in a closed system. As products of the process, a solid carbonaceous material, the hydrochar (HC), is obtained, as well a process water (PW), and a small fraction of gas (<5%) [6].

The knowledge gathered during more than one decade of intense worldwide research on HTC of biomass has shown, on the one hand, the potential of the process and its promising role to transform biomass into added value products with a wide range of applications but, on the other hand, also the complexity of the process, since a broad spectrum of reactions take place at different states of aggregation. We can classify them as processes:

- a) at the liquid-liquid interface to take place (products from HTC evolve or interact with others to form bigger compounds that can eventually form macromolecules or even solid nanoparticles (typically found as microspheres).
- b) at the liquid-solid interface, where adsorption reactions of some liquid compounds on the HC or deposition of the microspheres might take place.
- c) at the gas-liquid interface, where gasification processes of biomass/liquid fragments and gases (mainly CO₂) may also occur.

This complex interplay of processes determines the effect of time on the final HC mass, and therefore solid yield ($SY = \text{final HC mass} / \text{initial biomass mass}$) can increase or decrease with time depending on the reaction conditions (temperature) and the time range considered; it has to reach a particular value in order to guarantee the prominence of degradation reactions (and thus SY decreases with time), but if it is long enough it will involve a rise in SY because of the enhancement of recombination (condensation, polymerization) and adsorption processes.

On the other hand, the role of water is not still understood, and even less is how its participation (reactant and product) depends on the process conditions. While some clear water consuming and water producing processes are present at almost any reaction condition (hydrolysis and dehydration, respectively), the extent of polymerization and recombination reactions, and their influence on the water distribution has been scarcely tackled so far.

In order to give insight to this gap of knowledge, this study comprises a systematic research on the effect of water and time on the distribution of phases (solid and liquid) as well as on their properties. The extent of particular processes was suggested from the characterization results of hydrochars (surface morphology, point of zero charge, carbon densification and high heating value) and slurry (pH, conductivity and density).

2 Experimental

The raw material, pistachio nut shell (PNS) was provided by local farmers from the south west Spain Naval Moral de la Mata, Extremadura region) and subjected to crushing and grinding to get homogeneous particle size (1–2 mm). Thereafter, the material was dried in an oven to remove residual moisture in an furnace (120 °C). The procedure and characterization techniques used have been described in Fig. 1.

Experimental set-up

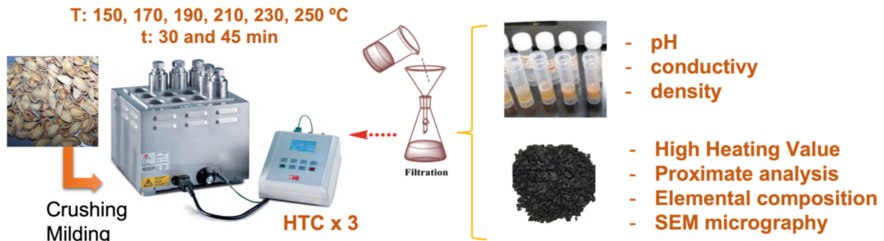


Fig. 1. Experimental procedure and characterization techniques

Hydrothermal carbonization processes (HTC) were performed on stainless steel vessel (Beghof DAB-2) that were inserted on an autonomous heating system. Water/biomass load, system volume and thermodynamical properties were designed to guarantee, in all cases, that water remained as liquid [7] (Ro et al., 2022). Temperature and time ranges of 150–250 °C and 30–45 min were used, respectively, while biomass/water ratio was in all cases 2:20 (wt./wt.%).

After processing, the reactor was opened, the gas vented, and the solid and liquid fractions weighed (paper filters had been previously weighed so that their contribution was then subtracted). Solid and liquid phases were characterized as follows:

- Hydrochar: Solid yield (SY, %), elemental analyses (EA-1108 CHNS (LECO Instrument), High Heating Value (HHV, 1351 Parr calorimetric bomb), Scanning Electron Microscopy (SEM, Quanta 3D FEG, FEI) and surface functionalization (FT-IR, Perkin Elmer model Paragon 1000PC spectrophotometer).
- Liquid: Liquid yield (LY, %), density, pH and conductivity (Crimson equipment).

3 Discussion of Results

Figure 2 compiles the solid yield (SY, %) evolution with temperature for some of the HTC reactions made under different dwell times. The moderate value of the lower temperature in the range (150 °C), which did not have any remarkable effect for 30 min (98.7%) was however enough to produce a clear degradation of biomass when the reaction time was further prolonged (87.4%, for 45 min sample).

This suggests that rather than HTC, 30 min reactions did only heated the biomass; heat transfer resistances along the several system layers (stainless steel reactor wall,

Teflon vessel wall and water) must have slow down the process. The 30 min heating for 150 °C run, however, did have any slight effect if one considers that the system pH dropped to 4.37 (initial pH around 7), so some pre-hydrolysis occurred, even under such mild conditions.

From our results, we can infer that since pH has already drop at 150 °C, hydrolysis is already taking place (at greater extent if longer times are used); this would in turn consume H_2O to form H_3O^+ ions. Then, dehydration can also happen, which would lead to the production of water. The temperature at which hemicellulose starts to decompose has been stated at about 180 °C [6], while cellulose decomposition has been placed at about 190 °C [8] (Sevilla et al., 2011) or 200 °C [6]. From our results, we already find a remarkable drop in SY at 170 °C. If these macromolecules are not still being degraded, then the SY drop could be associated to extractables.

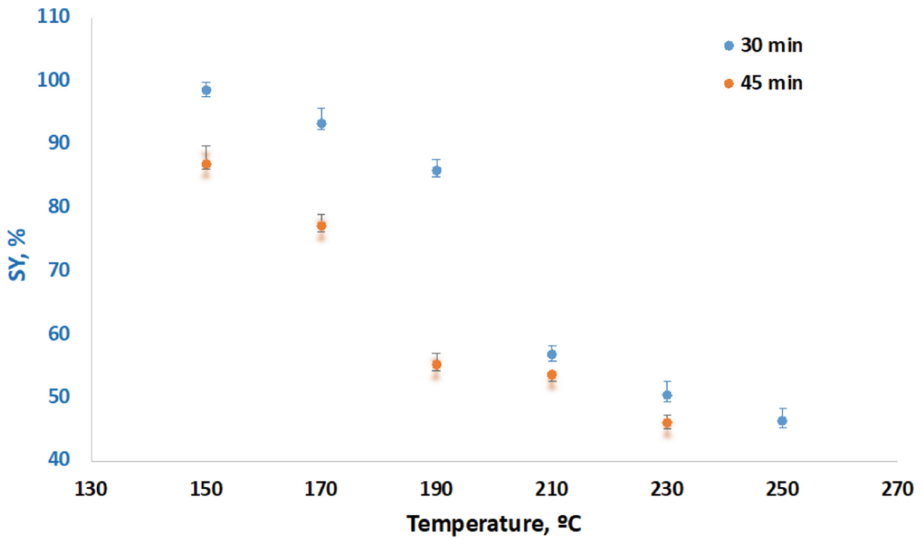


Fig. 2. SY values of HTC runs made under different temperature and time conditions

On the other hand, it is absolutely highlighting the cutting point we find in the range 190–210 °C, for which time elongation from 30 to 45 min passes from being significant to be not as much influent on the solid yield.

This might suggest that the reaction severity is mostly governed by temperature, but once a given temperature is used; this temperature, probably associated to cellulose breakage, will favour depolymerization reactions and thus the formation of monomers and oligomers. Whether these fragments are then combined on the liquid phase to yield other macromolecules that might then adsorb on the HC surface (and account for solid yield) is a fact difficult to prove, but the combined analysis of liquid and solid features can help, as we explain bellow.

Figure 3 shows the acidity values found on the liquid phase of each run. Following the previous approach, a greater reaction extension would also involve a rise on the H_3O^+ concentration at the liquid phase, since, by dehydration, the biomass carbohydrates such

as sucrose or starch, in their fundamental constituents (glucose and fructose) decompose to yield monomers and hydronium ions. The pH values in Fig. 3 (whose trend was opposite to slurry conductivity) also decrease with temperature and time (as it was found for SY) but the intensity of the decrease is rather constant (with the exception of longer times and greater temperatures).

This effect is in agreement with our previous hypothesis; the bigger the reaction severity, the greater the extent of degradation reactions, although prolonged time might a) favor secondary HC formation and, in a minor extent, c) favor acid consumption.

On the other hand, lignin from lignocellulosic biomass partially hydrolyses, giving rise to phenolic compounds [10]; although not shown here, previous results using the same raw material showed that increasing temperature involved an increasing formation of phenolic acids.

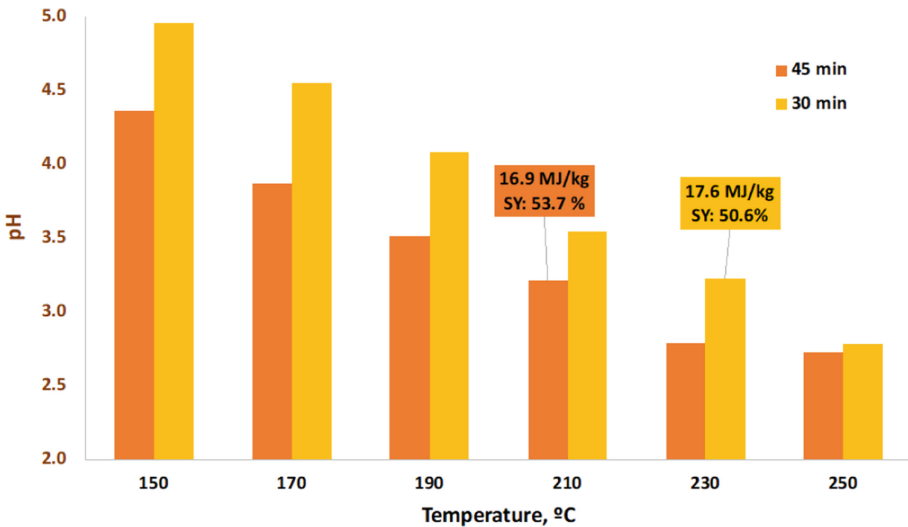


Fig. 3. Liquid pH values for runs made under different temperature and time conditions

In Fig. 3, the values of HHV (as representative of energy or carbon densification attained) and SY of specific runs have been included as labels. Having a look to these values, we can see that samples HC-210-45 and HC-230-30 show a similar value of HHV (16.9–17.6 MJ/kg) and also similar SY (53.7–50.6%), respectively. The pH for both is the same (3.23–3.21), suggesting that this value can be a good predictor of reaction severity and allow comparing experimental conditions. The experimental conditions used involve a rise on the HHV of the initial biomass (16.02 MJ/kg) up to 22.1 MJ/kg, and temperature was the factor with the biggest influence on it.

On the other, as expected, conductivity followed in all cases the opposite tendency of pH; it always increased with temperature and the range of values was in the interval 320–500 mV. It is outstanding that in absolute terms lower temperatures yielded lower values, suggesting a lower ionization of liquid phase due to less extent of hydrolysis.

One thing that has been scarcely studied so far regarding HTC processes is how experimental conditions can affect the liquid yield. This task has been often made by difference with the solid yield, assuming negligible gas yield (since it accounts for less than 5%, as most of the bibliography suggest).

In our case, we tried to quantify how much biomass fragments are transferred to the liquid phase by weighting the liquid phase (including the dried liquid volume) as well as the density of the slurry, and then estimating the mass gained by the water, making the corresponding mass balance.

The results for the series made during 30 min showed a clear tendency: greater temperatures have a positive effect on water formation; water was generated and in addition, the density was increased. This in turn indicates that a greater fraction of biomass was degraded, and the molecules transferred to the liquid phase were more abundant. This tendency, however, was not so clear at 45 min, what could be associated to the prominence of condensation and recombination reactions, that can favour the deposition of microspheres on the solid phase and this way decrease the liquid density.

These microspheres were identified by SEM micrography (Fig. 4), and were found to increase in size for longer times. The liquid for longer times also appeared clearer and less turbid.

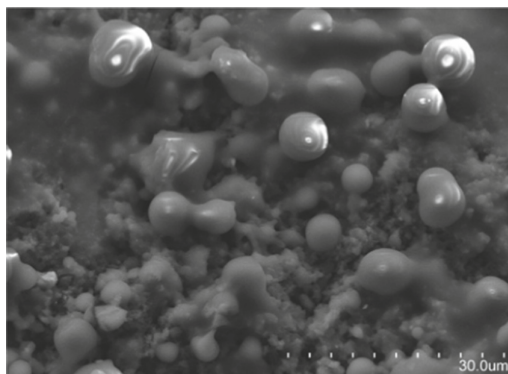


Fig. 4. SEM images of HC-230-30

Regarding the HCs surface properties, both the point of zero charge and surface functionalities were followed, and some of the most outstanding results have been plotted in Fig. 5.

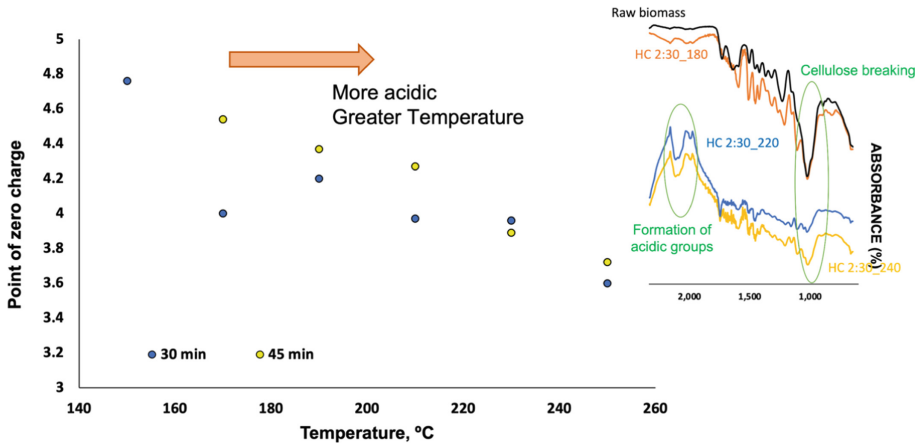


Fig. 5. Evolution of point of zero charge and FT-IR spectra

4 Conclusions

HTC experimental conditions (temperature and time) can yield carbon materials with a wide range of solid yield/energy densification and surface acidity. Both temperature and time affect the extent of HTC, although temperature seems to be more influential, especially at the first stages of the process, because it can define what degradation processes take place.

First pre-hydrolysis reactions already occur at 150 °C and 30 min of reaction, and the solid yield undergoes a continuous decrease up to 250°C, that is more intense as the heating is more severe in the range 170–190 °C, coincident with the cellulose breaking, which was further identified from surface FT-IR spectra. All these have an immediate effect on the hydronium ion concentration of the liquid phase at the same time that it gets denser as a lot of monomers are formed as a result of polymer breaking up.

Further degradation processes (decarboxylation, decarbonylation or demethanation) and decomposition of these monomers involve the formation of acids that can combine and yield other compounds (eventually, larger times can result on a rise on liquid pH) and even water molecules can form. Besides, time can also favor the adsorption of molecules from the liquid phase so that final water density drops and solid yield increases.

Future works will be devoted to analyzing the composition of water during and after HTC processes.

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References

1. European Green Deal: European Commission (2019–2024). https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_es
2. Spanish Pistachio Industry report 2022-2026. <https://www.reportlinker.com/report-summary/Agricultural-Products/146666/Spanish-Pistachio-Industry.html?tstv=no-test>
3. Xu, S.-D., et al.: Curly hard carbon derived from pistachio shells as high-performance anode materials for sodium-ion batteries. *J. Mater. Sci.* **53**(17), 12334–12351 (2018). <https://doi.org/10.1007/s10853-018-2472-4>
4. Hassan, A.F., Youssef, A.M., Priece, P.: Removal of deltamethrin insecticide over highly porous activated carbon prepared from pistachio nutshells. *Carbon Lett* **14**, 234–242 (2013)
5. Fernández-Sanromán, A., et al.: Bridging the gap to hydrochar production and its application into frameworks of bioenergy, environmental and biocatalysis areas. *Biores Technol.* **320**, 124399–124408 (2021)
6. Reza, M.T., Uddin, M.H., Lynam, J.G., Hoekman, S.K., Coronella, C.J.: Hydrothermal carbonization of loblolly pine: reaction chemistry and water balance. *Biomass Conv. Bioref.* **4**(4), 311–321 (2014). <https://doi.org/10.1007/s13399-014-0115-9>
7. Ro, K.S., Libra, J.A., Alvarez-Murillo, A.: Comparative studies on water- and vapor-based hydrothermal carbonization: process analysis. *Energies* **13**(21), 5733 (2022)
8. Sevilla, M., Fuertes, A.B.: The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* **47**, 2281–2289 (2009)
9. Fakkaew, K., Koottapek, T., Polprasert, C.: Effect of hydrolysis and carbonization reactions on hydrochar production. *Biores. Technol.* **192**, 328–334 (2021)
10. Baruah, J., et al.: Recent trends in the pretreatment of lignocellulosic biomass for value-added products. *Front. Energy Res.* **18**(141), 1–19 (2018)



Post-treating Biomass Hydrochars to Improve Their Suitability at Soil Amendment

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Abstract. Hydrothermal carbonization has been proven to be an effective way of densifying the carbon content of biomass; at the same time, the resulting carbon material (hydrochar, HC) has porosity properties that can help the transport of water and nutrients in soil amendment applications. There is, however, evidence that the presence of some surface compounds on the HCs can have a detrimental effect on the soil physico-chemical properties and in consequence also on plant growth.

This study aimed to improve the performance of walnut shell HCs in this application, by subjecting them to hot water, acetone and hydrochloric acid washing. In addition, the effect of the addition of these HCs on agricultural soil was evaluated under different proportions (1%, 3% y 9%). The results showed that both growing and germination indexes of lettuce plants were improved after HCs were treated; also, it was found that using a high concentration of material make the substrate phytotoxic.

Keywords: Soil amendment · Fertilizer · Hydrothermal carbonization

1 Introduction

Agriculture faces today several significant challenges such as climate change, soil degradation and loss of fertility. Moreover, demographical growing also causes deficiencies on food supply, what is mitigated by abusive and not sustainable techniques based on the excessive use of fertilizers and intensive managing, which also contributes to soil contamination [1].

The severe effects of agriculture on climate change can be associated to anthropogenic carbon dioxide emissions (10–12% of the yearly worldwide emissions) [2] and to most of nitrogen oxides from soil microbial activity and the massive use of nitrogenated fertilizers [3]. In addition to soil degradation due to agricultural activities, its

contamination because of industry practices is even more drastic (discharge of chemicals, heavy machinery, over exploitation of hydric resources, etc.). It is therefore essential to promote short-term sustainable agricultural practices and, in this line, the use of organic wastes as substrates (or part of it) has a main role.

A substrate can be defined as any solid material different to soil, that can be natural or synthetic, mineral or organic, and can be added as a pure material or blended. The main functions of the substrate are generally providing plant anchorage, and delivering water, nutrients, and oxygen to the roots.

Cultivation on substrate provides, in relation to soil farming, a greater control in relation to the production factors of the plant radical system. The volume the roots must follow is reduced by using substrates, that also have the ability of retaining water at low strain stress. This ability, related to the particle size (bigger than in soils), allows the elimination of water from the pores under low strains [4]. Substrates also favor nutrient transport and air diffusion within the soil matrix.

Biochars (chars from pyrolysis, also called pyrochars) have been used as substrates during many years. As a result of pyrolysis, the C from biomass is stabilized and becomes more resistant to chemical and biological decomposition [5]. Adding biochar to soil reduces its apparent density, increases its water retention capacity and improves the soil structure [6]; it also enhances its infiltration and permeability capacity, which results in a better development of roots and microbial breathing as well as gas exchange.

Hydrochars (HCs) are carbon materials that share some characteristics with biochars. In the first place, HCs are obtained following a much more sustainable process, hydrothermal carbonization (HTC), also called wet pyrolysis. HTC requires mild temperatures (around 180–250 °C, instead of 600–800 °C of pyrolysis) and also enables the use of wet biomass; since water is a reactant of the process, the water content of the precursor is no longer a problem, as it happens with pyrolysis (this is an outstanding point since it allows broadening the scope of potential raw materials to humid biomass, sewage sludge, manure, and others).

HTC can be regarded as a CO₂ capture process, since most is the carbon that was fixed by the plants during its photosynthesis is recovered into the solid product (the hydrochar), accumulated in a material that resists natural processes of degradation that would otherwise release this carbon dioxide again; it therefore represents an artificial way of fixing carbon of biomass on a large scale. In addition, HTC process does not need costly drying pretreatments since the water of the precursor is used as a reactant in the process [7].

As detrimental aspects in relation to pyrochars applied to soil amendment processes, HCs in general present fewer aromatic structures on its surface, greater H/C ratios, are more unstable and can have surface acid groups. As advantage, HCs are associated with a faster mineralization, a lower content of heavy metals and better cation-exchange capacity (CEC).

There are very few studies on the use of biomass HCs in this application are controversial; some point out its potential as nutrient source some others allude to its toxicity; there is a lack on the systematic study of HCs added to real soil.: Bejarano and Aguilar [7] reported that the HC rapidly improved the soil properties due to the fast mineralization, what involved a better C fixation, pH and CEC. Differently, Gronwald et al., [8]

found that C sequestration was poorer for HCs, but highlighted their potential to act as a mid-term fertilizer through slow nutrient release to soils.

Within this framework we aim to evaluate the fitotoxic activity of different types of HCs; namely: simple walnut shell HC (HC), HC washed with distilled water (HCL) and HC washed with acetone (HCLA). The study aims to evaluate the fitotoxic activity of walnut shell HCs, under different concentrations, on the germination, root length and stem length of the plant *Lactuca sativa*.

2 Experimental

2.1 Hydrochar Preparation

Hydrochars (HCs) were made from walnut Shell, provided by local farmers (Benavides plantation, property of Borges, Olivenza, Spain) and was subjected to grinding and sieving to a particle size of 1–2 mm. HCs were prepared in a stainless steel autoclave according to the procedure described in ref. [9] at 230 °C during 20 h. As a result of the process, a slurry composed of liquid oily phase and HC.

Three different fractions of HCs were used: HCs resulting from the separation of the slurry by simple filtration on Whatman paper, b) HC washed with acetone and c) HC washed with hot water (300 mL, 4 times). After these processes, the HCs were dried at 110 °C overnight.

2.2 Field Incubation Tests

Commercial lettuce seeds (*Lactuca sativa* L. variedad Romaine Verte Maraichère) were used in this study, due to their high sensitivity.

The substrate was obtained from an area placed at southern Spain, characterized by dry soil (Luvisol albi-gleic type, coordinates 38.885559 –7.015051); Surface layers up to 5 cm deep were gathered (5 kg). Filter paper (Whatman n° 118, 90 mm diameter).

The substrate, universal type, has the following properties: organic/dry matter: 60%, electrical conductivity: 40 mS/m, apparent dry density: 320 g/l, granulometry: 0–20 mm and pH: 6,5.

The biotests were static test of acute toxicity with a duration of 5 days each. Germination of the seeds and growing of the plants during the first days were evaluated, as well as the inhibition on the germination, the emergence of cotyledons, and hypocotyl by the estimation of several characteristic indexes.

In each bio-assay, 50 seeds were placed on Petri plates with 50 g of substrate, that was a blend of commercial substrate and HC under different proportions (1, 3 and 9% wt.); each run was made four times. The samples were kept during 5 days on a germination chamber at 21 °C with a 12 h light/ 12 h darkness photoperiod. All plates were watered on the first day with 20–25 ml of distilled water.

3 Discussion of Results

Figure 1 shows the effect of the HC addition on the germination of *Lactuca sativa*. At first glance, it can be deduced that adding non-washed HC inhibits the germination, and

this effect is significant when the HC is added in a greater quantity (9% run). A very different trend is found when the HC is subjected to washing both with hot water or acetone: in these cases, total germination and its speed are greater than the control test; especially, the HCLA-9% shows a significant improvement.

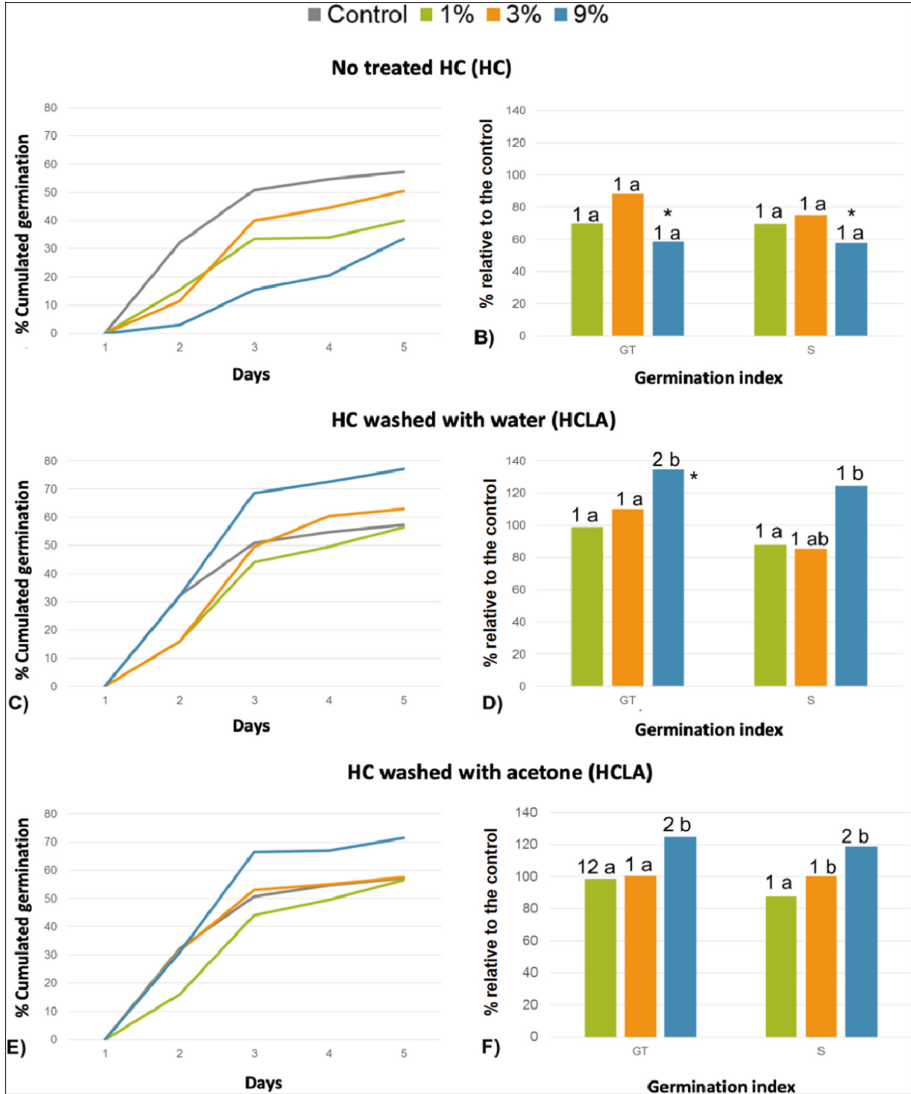


Fig. 1 Percentage of daily germination accumulated and percentage relative to the control of total germination (GT) and velocity speed (S) of *Lactuca sativa*. * significantly different to control: $p < 0,05$ (Mann-Whitney U-test). a, b y c: different letters indicate significant differences between HCs. 1, 2 y 3: different numbers indicate significant different between concentrations

This result is consistent with the data related to the days needed for the germination of 50% of the seeds (T_{50}), included in Table 1. When non-washed HC is used, more days are needed (or this germination percentage is not even reached). After treatment, this time period is decreased until the level of the control sample.

Table 1. T_{50} results (days) for different HCs

		1%	3%	9%
Control	3			
HC		-	5	-
HCL		5	4	3
HCLA		5	3	3

In relation to total germination (GT) in percentage relative to control, it was found that, as the percentage of washed HC is greater, the number of germinated seeds increased, and there are significant differences in relation to control sample, up to 134% (when the concentration of HCL is 9%). For 3% run, the number of germinated seeds also surpasses the control run (120%) and in the case of 1% the effect is low. Figure 2 shows some images corresponding to the germination tests of HCLA, the last day of the run.

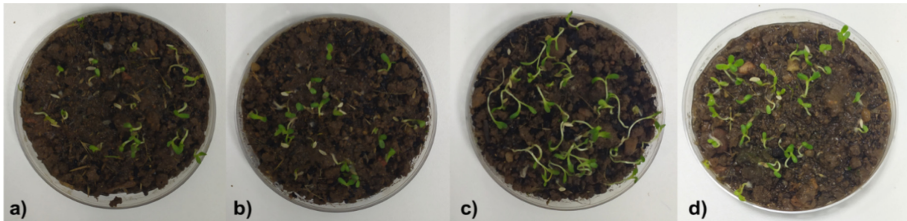


Fig. 2 *Lactuca sativa* showed on soil with a substrate enriched with HC washed with distilled water (HCLA) at different concentrations: a) 1%, b) 3% y c) 9%; d) control plate without HCLA

4 Conclusions

The results obtained showed that hydrochar pretreatment was decisive on its effect on the soil and plant growing parameters. In this way, the higher load of hydrochar without washing, the greater the inhibition of germination and development of *Lactuca sativa*. In contrast, when hydrochar washed with water and hydrochar washed with acetone were used, a greater load of hydrochar brought up a greater germination, and growth of the plants.

The fact that washed HCs contribute to an improvement of *Lactuca sativa* germination demonstrates that they can mean a new soil improver, much more sustainable

than traditional fertilizers, and can at the same time be a tool to fight against the climate change.

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References

1. Cabrera, R.I.: Manejo de sustratos para la producción de plantas ornamentales en maceta. 2º Simposio Nacional de Horticultura. Memorias. Universidad Autónoma Agraria Antonio Narro, p. 9. Saltillo, Coahuila, México (2002)
2. Stern, D.I., Kaufmann, R.K.: Anthropogenic and natural causes of climate change. *Climatic Change* **122**, 257–269 (2014)
3. Smith, P., et al.: Agriculture, forestry and other land use. In: Edenhofer, O., et al. (eds.) Cambridge University Press. United Kingdom, New York, NY, USA, Cambridge (2014)
4. Moreno, J.M.A.: La materia orgánica y la capacidad de retención de humedad en sustratos. *Agric. Org.* **1**, 23–25 (2002)
5. Lehman, J., Joseph, S.: *Biochar for Environmental Management*. Earthscan Publishers, United Kingdom (2009)
6. Baronti, S., et al.: Impact of biochar application on plant water relations in vitis vinifera (L). *Eur. J. Agron.* **53**(38), 44 (2014)
7. Moreno, L.M.B., Díaz, P.A.A.: Evaluación del biochar e hidrochar como medios para captura de carbono en el suelo. Universidad de La Salle. Facultad de Ingeniería. Ingeniería Ambiental y Sanitaria (2017). https://ciencia.lasalle.edu.co/ing_ambiental_sanitaria/710
8. Gronwald, M., Vos, C., Helfrich, M., Don, A.: Stability of pyrochar and hidrochar in agricultura soil—a new field incubation method. *Geoderma* **284**, 85–92 (2016)
9. Román, S., Nabais, J.M.V., Laginhas, C., Ledesma, B., González, J.F.: Hydrothermal carbonization as an effective way of densifying the energy content of biomass. *Fuel Process. Technol.* **103**, 78–83 (2012)



Antioxidant Activity and Nutritional Composition of Fine Grounds Obtained in the Production of Sour Cherry Liqueur: A By-Product Valorization

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Abstract. Fine grounds are one of the by-products resulting from the production of sour cherry (*Prunus cerasus*) liqueur, obtained by decanting the liquor when it is in the storage stage. These consist of a portion of solid material, from plant origin, which is suspended in a sugary hydroalcoholic solution. As a by-product, it is currently undervalued, namely in the food sector. Aiming to find a possible use for this by-product, nutritional characterization of the fine grounds was carried out regarding protein, lipid, carbohydrate, and ash contents, as well as the fatty acid (FA) profile. Also, the antioxidant activity of extracts was evaluated. The analyses were done on the dry residue containing 18% humidity, obtained by centrifugation followed by drying the solid residue at 30°C. Fine grounds were mainly constituted by carbohydrates (57.81%) and proteins (17.64%) and, in lower values, by lipids (4.66%) and ash (1.82%). Polyunsaturated fatty acids were the major class corresponding to 43.9%, whereas saturated and monounsaturated fatty acids appeared in similar amounts corresponding to 29.8% and 26.3% of total FA, respectively. Oleic (C18:1 n-9) and linoleic (C18:2 n-6) were the most abundant FA, reaching values of $25.62 \pm 0.11\%$ and $22.32 \pm 0.08\%$, respectively. No relevant antioxidant activity was observed in the extracts prepared by sequential extraction with solvent increasing polarity. Due to its balanced nutritional composition, the valorization of fine grounds could be done through its use as an additive to flour or as a powder used to flavour various beverages, yogurts, and similar products.

Keywords: By-product valorization · Fatty acids · Nutritional composition · Sour cherry · Sour cherry liquor

1 Introduction

Solid waste management has become one of the major environmental concerns in the world. In 2006, the European Union generated around 89 million tons of food waste

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without any valorization [1]. According to the circular economy development model, it is possible to build a more harmonious society that efficiently manage all natural resources in a sustainable way, by increasing the recovery and recycling of by-products and materials, and their conversion into new and low-cost interesting products [2].

In recent years, some of the industrial waste and by-products have been studied to evaluate their nutritional composition and the presence of bioactive compounds. In fact, these by-products showed enormous potential as source of compounds with antioxidant, and antimicrobial activities that might have interest to pharmaceutical, food, agriculture, or cosmetic industries [3–5].

Sour cherry, (*Prunus cerasus* L.) is an acidic fruit that, due to its bitter taste, is not used for direct consumption. However, it is widely used for liquor production that can be found in many countries of Europe, namely in Portugal, and of Southwestern Asia. In the manufacturing process, fruits are first infused in an alcoholic solution to extract aromatic and color compounds, and afterwards pressed to separate the pomace from the suspension. Then, the suspension is mixed with sugar syrup and left to decant to separate the liquor from the fine solid residue. Therefore, the production of this liquor generates substantial amounts of direct (pomace and fine grounds) and indirect (stems and leaves) solid waste [6].

In the last few years, several studies have showed that sour cherry is rich in bioactive compounds, due to its phenolic and flavonoid contents, and has high nutritional value [7–12]. The bioactive compounds identified in this fruit can also provide important health benefits, such as antioxidant, anti-inflammatory, and anticancer properties [7, 13–16]. Thus, it is likely that the waste obtained from the production of sour cherry liquor has important bioactivities and/or high nutritional value.

Many authors have studied the phytochemical composition of pomace, skin, stones, leaves and stems of sour cherry. Piccirillo et al. [17, 18] have reported that ethanolic extracts from both stems and leaves of sour cherry plants were rich in polyphenols and showed antibacterial activity against several bacterial strains (both Gram-positive and Gram-negative species). These results are in agreement with those obtained by Demiray et al. [19] who described the highest antioxidant properties in 70% ethanol stems extract and in pure water leaves extracts. Maurício et al. [20] tested the pomace and skin of sour cherry, obtaining the highest extraction yield, polyphenolic content, and antioxidant activity in the skin samples. Also, Yılmaz et al. [21] reported the composition, functional properties, and recovery potential of by-products of sour cherry. It is referred that the pomace and seeds of sour cherry have antioxidant activities and contain valuable amounts of biological compounds that could be recovered for new functional food development. However, to the best of our knowledge, the biological potential of the fine grounds, a by-product of the production of sour cherry liquor, has never been evaluated.

Thus, this study aimed to evaluate the nutritional composition of fine grounds (FG), obtained after decantation of sour cherry liquor, the phenolic content, and the antioxidant activity of extracts, prepared by sequential extraction following increase solvent polarity, in order to develop a novel functional food with relevant biological properties.

2 Materials and Methods

2.1 Sample Preparation

Fine grounds (FG) were obtained by centrifugation at 12000 rpm for 10 min (Eppendorf, Hamburg, Germany). The solid residue was dried at 30 °C for 48 h and subsequently homogenized, originating a dry residue (DR). The DR was characterized regarding its nutritional composition, fatty acid profile, and extracts antioxidant activity.

2.2 Nutritional Composition

Water Content. Water content was determined according to the method 930.15 of AOAC [22]. DR samples (3 g) were weighed into porcelain crucibles, which were previously dried at 500 °C (Nabertherm, Bermen, Germany) for 4 h. The crucibles containing the DR samples were then dried in an oven (BINDER, Tuttlingen, Germany) at 105 °C, until constant weight. Samples were analysed in quadruplicate and the results were expressed as % of DR.

Ash Quantification. Mineral content quantification was performed according to the method 955.04 of AOAC [22]. Samples previously dried at 105 °C were incinerated in a muffle (Nabertherm, Bermen, Germany) at 500 °C for 12 h. Results were expressed as % DR or % of dry weight of dried residue (% DW).

Total Protein Content. Total protein of the DR was quantified from the total nitrogen content, determined by the Kjeldahl method, protocol nr. 978.04 of AOAC [22] as described by Neves et al. [23], using a conversion factor of 6.25. Samples were analysed in quadruplicate and the results were expressed as % DR and % DW.

Total Lipid Content. Total lipid content was determined according to Folch et al. [24] with slight modifications described by Neves et al. [23]. Samples were analysed in quadruplicate and the lipid content was expressed as % DR and % DW.

Total Carbohydrates Content. Total carbohydrates (% DW) were determined by difference, considering total protein, total lipids, and ash values.

2.3 Fatty Acid Profile

Firstly, dry residue samples were directly transmethylated to obtain fatty acid methyl esters (FAME), as described by Fernández et al. [25]. FAME were analysed by gas chromatography (GC) following the procedure described by Neves et al. [23] with differences in the oven temperature program of the Finnigan Trace gas chromatographer Ultra (Thermo Electron, Waltham, Massachusetts, EUA) that was programmed as follows: set at 100 °C for 0.1 min, followed by an increase at 10 °C/min to 150 °C (maintaining for 1 min), a second increase at 5 °C/min to 200 °C (during 9 min) and finally an increase at 2 °C/min to 235 °C (during 5 min). Fatty acids were identified by comparison of its retention time with those of Supelco 37, PUFA 1 and PUFA 3 standard mixtures. The

results were expressed as percentage in respect to total area (% Total FA) and the amount of each fatty acid ($\mu\text{g}/\text{mg}$ DR) was calculated by the internal standard method, according to the following equation:

$$FA_x(\mu\text{g}/\text{mg}) = \frac{\text{Area}(FA_x)}{\text{Area}(IS)} \times \frac{V_{IS} \times C_{IS}}{V_E} \times \frac{V_S}{m_s} \times \frac{RRf}{K} \quad (1)$$

Being: FA_x – The fatty acid to be quantified; IS – Internal standard; C_{IS} – Concentration of IS ($\mu\text{g}/\text{mL}$); V_{IS} – Volume of IS solution added in the vial (μL); V_E – volume of sample hexane extract added in vial (μL); V_S – volume of hexane used for the extraction of FAME from samples (mL); m_s – mass sample (mg); RRf – Theoretical relative response factor related with the IS (C17 FAME) [26]; K – FAME/FA mass ratio.

In addition, the thrombogenic index (TI), atherogenic index (AI) and hypocholesterolemic/hypercholesterolemic fatty acids index (H/H) were calculated according to the following equations:

$$TI = \frac{C14 : 0 + C16 : 0 + C18 : 0}{0.5 \times \sum MUFA + 3 \times \sum n3 + 0.5 \times \sum n6 + \frac{\sum n3}{\sum n6}} \quad (2)$$

$$AI = \frac{C12 : 0 + 4 \times C14 : 0 + C16 : 0}{\sum MUFA + \sum n3 + \sum n6} \quad (3)$$

$$H/H = \frac{C18 : 1n9 + C18 : 2n6 + C20 : 4n6 + C18 : 3n6 + C20 : 5n3 + C22 : 5n3 + C20 : 6n3}{C14 : 0 + C16 : 0} \quad (4)$$

2.4 Extracts Characterization

Extraction Procedure. Dry residue (100 g) was used for sequential extractions with 1L of each solvent, following increase polarity, as follows: petroleum ether (PE), acetone (Ace), ethanol (EtOH), ethanol 50% (EtOH 50%) and water (Wt), under stirring at room temperature for 3 h. After each extraction, the extracts were filtered, and the solvents were removed by vacuum evaporation (IKA, Staufen, Germany). Finally, the three less polar extracts were dried in an oven at 30 °C and the remaining were lyophilized. All extracts were characterized in terms of antioxidant activity and phenolic profile.

Total Phenolic Content. Total phenolic content (TPC) quantification of the dry residue extracts was performed spectrophotometrically (at 755 nm, BioTek Instruments, Winooski, USA) according to the Folin-Ciocalteu colorimetric method [27] adapted to the micro-scale as described by Neves et al. [23]. The results were expressed as μg gallic acid equivalent per mg of dry extract (DE) (μg GAE/mg DE).

DPPH Scavenging Activity. The DPPH radical scavenging activity of the extracts was evaluated as described by Neves et al. [27] with some modifications. In Eppendorf tubes, were added 950 μL of DPPH solution (40 $\mu\text{g}/\text{mL}$ of ethanol) and 50 μL of extract (1 mg/mL) dissolved in their extraction solvent. The samples were stirred and

kept in dark at room temperature for 30 min. Posteriorly, four aliquots of 200 μL of the mixture were transferred to a 96 well microplate and the absorbance was measured at 517 nm (BioTek Instruments, Winooski, USA). Solutions of the synthetic antioxidant Trolox was subjected to the same process, as well as the solution used as negative control (consisting of 950 μL of DPPH and 50 μL of the dissolution extract solvent) and blanks (950 μL of ethanol and 50 μL of each extract). The results were expressed as μg Trolox equivalent per mg of DE (μg Trolox/mg DE).

Ferric Reducing Activity Power (FRAP). The evaluation of the antioxidant activity by the Fe (III) reducing power was performed spectrophotometrically (595 nm, BioTek Instruments, Winooski, USA) and adapted to a microscale according to Neves et al. [23]. Standard solutions of Trolox were used for the elaboration of the calibration curves. The results were expressed as μg Trolox/mg DE.

ABTS Scavenging Activity. Antioxidant activity of the extracts was also evaluated by the ABTS scavenging activity assay, as described by Konan et al. [28]. ABTS reagent was previously prepared by mixing 7 mM $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_6\text{S}_4\text{-(NH}_4)_2$ and 12.25 mM $\text{K}_2\text{S}_2\text{O}_8$ in a proportion of 4:1. After 16 h in the dark, the absorbance of the solution was adjusted to 0.700 at a wavelength of 734 nm (Thermo Fisher Scientific, Shanghai, China). The color reaction was carried out in Eppendorf tubes, adding 50 μL of extract (1 mg/mL) and 950 μL of ABTS reagent. After stirring for 1 min, the samples were transferred to a cuvette and the absorbance was measured at 734 nm. The analyses were performed in triplicate. The same procedure was used for the blanks and standard solutions. Calibration curves were prepared with Trolox standard solutions. The results were obtained in μg Trolox/mg DE.

2.5 Statistical Analysis

All experiments were conducted in at least three independent replicates and the presented values correspond to the mean \pm standard deviation. Statistical tests were done with the SPSS software 28 (IBM Corporation, USA). The results were considered statistically significant with a significance level of 5%. The data were analysed by analysis of variance (one - way ANOVA). The assumptions of ANOVA were verified through the Kolmogorov-Smirnov normality test and Levenne homogeneity. Depending on the fulfilment of the ANOVA assumptions, Tukey's or Games-Howell's multiple comparison tests were applied.

3 Results and Discussion

3.1 Nutritional Composition

The centesimal composition of the FG dried residue (DR) is presented in Table 1. The nutrient present in highest amount were carbohydrates (*c.a.* 58%), followed by water, proteins, lipids, and ash. Regarding macronutrients, DR has a balanced composition, containing approximately 344 kcal/100 g. The energetic distribution of macronutrients

Table 1. Proximate composition (% DW and % DR) and macronutrients energy value of the dried residue.

Parameters	Content			
	Dry weight of dried residue (%)	Dried residue (%)	Energy (Kcal)	Total energy value (%)
Protein	21.51 ± 0.17	17.64 ± 0.14	71	21
Fats	5.69 ± 0.04	4.66 ± 0.04	42	12
Ash	2.22 ± 0.03	1.82 ± 0.13	n.a	n.a
Carbohydrates	70.57 ± 0.19	57.81 ± 0.33	231	67
Water content	0	18.06 ± 0.33	n.a	n.a

n.a.- not applicable.

relative to the total energy value, existing in DR, is very to the Eurodiet Core Report 2000 and the FAO/WHO 1990 recommendations, being 55% to 75% for carbohydrates, 15% to 30% for lipids and 10% to 15% for protein [29].

The fatty acid profile determined by gas chromatography is shown in Table 2. The main FA found was oleic acid, a monounsaturated FA (C18:1 n-9 cis), followed by the polyunsaturated FAs linoleic acid (C18:2 n-6) and alpha-linolenic acid (ALA) (C18:3 n-3). The most abundant saturated FA were palmitic (C16:0) and lauric acid (C12:0). It was not possible to identify the sixth most abundant compound, which is about five times lower than the oleic acid content. Through bibliographic research, we suggest that it may be the alpha-eleostearic acid (C18:3 n-5) [30, 31]. The seventh most abundant FA was stearic acid (C18:0). The remaining FA are minority shareholders, with percentages lower than 1%. In oil obtained from cherry pits (*Prunus avium* L.) it is possible to find a constitution of FA like that found in DR, however it is verified that in cherry kernels oil, the proportion of alpha-eleostearic acid appears in third place, followed by linoleic and oleic acids with increasing concentrations. The fourth most abundant FA, in cherry oil, it is palmitic acid [30].

Aiming the evaluation of food nutritional value and its health effect, PUFA/SFA and n-6/n-3 ratios as well as thrombogenic (TI), atherogenic (AI), and hypocholesterolemic/hypercholesterolemic (H/H) fatty acids indexes are frequently used [32–34]. Values of PUFA/SFA higher than 0.4 and n-6/n-3 ratio lower than 4.0, in human diets, are recommended to prevent the development of cardiovascular diseases and some chronic diseases, such as cancer [33, 35]. In FG, PUFA/SFA and n-6/n-3 had values of 1.47 and 1.34, respectively (Table 2). Being in accordance with the recommended values, FG appear to be a healthy source of fatty acids. Also, a fatty acid source is considered a healthy one, with potential protective effect for coronary artery disease, if low AI and TI (<1.0 and <0.5, respectively) and high H/H indexes occur [34, 35]. The AI indicates the ratio between the sum of the main SFA and that of main classes of UFA, the former being considered proatherogenic (favouring the adhesion of lipids to cells of the immunological and circulatory system), and the latter being antiatherogenic (inhibiting the aggregation of plaque and diminishing the levels of esterified fatty acid, cholesterol,

Table 2. Fatty acid profile of the dried residue.

Fatty acid	Total fatty acids (%)			Concentration ($\mu\text{g}/\text{mg}$)		
		\pm			\pm	
C12:0	9.63	\pm	0.10	2.14	\pm	0.15
C14:0	0.33	\pm	0.03	0.07	\pm	0.01
C15:0	0.19	\pm	0.02	0.05	\pm	0.00
C16:0	15.64	\pm	0.09	3.64	\pm	0.33
C17:0	0.35	\pm	0.02	0.08	\pm	0.01
C18:0	3.38	\pm	0.04	0.79	\pm	0.08
C20:0	0.29	\pm	0.03	0.06	\pm	0.01
C16:1 n-7	0.7	\pm	0.06	0.18	\pm	0.03
C18:1 n-9 cis	25.62	\pm	0.11	5.93	\pm	0.48
C18:2 n-6	22.32	\pm	0.08	4.99	\pm	0.53
C18:3 n-3 (ALA)	16.68	\pm	0.04	3.87	\pm	0.33
C18:3 n-5	4.86	\pm	0.05	1.09	\pm	0.08
Σ SFA	29.82	\pm	0.13	6.82	\pm	0.56
Σ MUFA	26.32	\pm	0.07	6.12	\pm	0.50
Σ PUFA	43.86	\pm	0.08	9.95	\pm	0.93
Σ UFA	70.18	\pm	0.13	16.06	\pm	1.42
Σ n-3	16.68	\pm	0.04	3.87	\pm	0.33
Σ n-6	22.32	\pm	0.08	4.99	\pm	0.53
UFA/SFA	2.35	\pm	0.01	n.a		
PUFA/SFA	1.47	\pm	0.01	n.a		
n-6/n-3	1.34	\pm	0.01	n.a		
H/H	4.05	\pm	0.03	n.a		
AI	0.41	\pm	0.00	n.a		
TI	0.26	\pm	0.00	n.a		

n.a.- not applicable. SFA – Saturated Fatty Acids; MUFA – Monounsaturated Fatty Acids; PUFA – Polyunsaturated Fatty Acids; UFA – Unsaturated Fatty Acids; H/H – Hypocholesterolemic/Hypercholesterolemic fatty acids index; AI – Atherogenic index; TI – Thrombogenic index.

and phospholipids, thereby preventing the appearance of micro-coronary and macro-coronary diseases). The TI values indicate the tendency to form clots in the blood vessels. This is defined as the ratio between the prothrombogenic (saturated) and antithrombogenic fatty acids (Σ MUFA, n-6, and n-3) [36]. The ratio between hypocholesterolemic and hypercholesterolemic fatty acids (H/H) indicates the effects of specific fatty acids on cholesterol metabolism. Nutritionally higher H/H values are considered more beneficial for human health [35]. Considering the recommended values for AI, TI, and H/H,

which values were 0.41, 0.26 and 4.05, respectively, one may conclude that the FG is a by-product with a healthy and balanced fatty acid profile.

3.2 Extracts Characterization

The results for the total phenolic content and antioxidant activity are shown in Table 3. Ethanol 50% and water extracts showed the highest phenolic content and antioxidant activity, with exception on ABTS assay. Water extract had the highest values in TPC (77.63 $\mu\text{g GAE/mg}$) and in FRAP assay (40.0 $\mu\text{g TroloxE/mg}$). These values showed significant differences when compared to the remaining extracts. Conversely, the hydroethanolic extract had the highest antioxidant activity in the DPPH and ABTS assays (41.8 and 27.95 $\mu\text{g TroloxE/mg}$, respectively) with significant differences comparing to the other extracts. In opposition, ethanolic extract showed the lower antioxidant activity and petroleum ether extract did not show any antioxidant activity in any of the tested methods. Overall, it is not visible a higher phenols content or antioxidant activity in all the five extracts. It is possible that the higher amounts of phenolic compounds with antioxidant properties might be in the liquor, the hydroalcoholic extract of sour cherry.

Table 3. Total phenolic content (TPC) expressed as gallic acid equivalents ($\mu\text{g GAE/mg}$); DPPH scavenging activity, ABTS scavenging activity and FRAP expressed as ($\mu\text{g TroloxE/mg}$);

Parameter	Sour cherry extract				
	Petroleum ether	Acetone	Ethanol	Ethanol 50%	Water
TPC	1.9 \pm 1.4 ^a	12.98 \pm 0.89 ^b	5.38 \pm 0.00 ^c	47.01 \pm 0.89 ^d	77.63 \pm 0.69 ^e
DPPH	8.5 \pm 3.4 ^a	13.5 \pm 2.3 ^b	11.8 \pm 2.1 ^{a,b}	41.8 \pm 3.1 ^c	30.0 \pm 2.8 ^d
ABTS	6.2 \pm 3.2 ^a	5.79 \pm 0.40 ^{a,b}	5.43 \pm 0.21 ^{a,b}	27.95 \pm 0.73 ^c	2.02 \pm 0.76 ^b
FRAP	*	12.00 \pm 0.76 ^a	6.87 \pm 0.31 ^b	32.17 \pm 0.15 ^c	40.0 \pm 2.2 ^d

* Without activity. On the same row, different letters mean significant differences ($P < 0.05$) between extracts.

4 Conclusions

By analysing the nutritional values obtained during the study, it is notable that it can be used in the production of a novel product or as a food supplement. In fact, with reference to Regulation (EC) no. 1924/2006 of the European Parliament [38] this product could have the nutrition claim “Source of protein” or “High protein content”, as it contains more than 12% of the total energy value supplied by proteins (21%). Concomitantly, the DR could contain the claim “Low in saturated fat”, since it does not exceeds 1.5g/100g of saturated fatty acids and fatty acids trans. In addition, it was noteworthy that the fat content of the DR of FG has a healthy composition, with an UFA/SFA, PUFA/SFA and n-6/n-3 ratios and thrombogenic, atherogenic and hypocholesterolemic fatty acids

/ hypercholesterolemic fatty acids indexes, within the recommended values. However, the phenolic content and antioxidant activity of the tested extracts despite being present, did not show significant values. The pigments present in DR have not been studied in this work, however, there is also a potential for its recover and use.

References

1. European Environment Agency: Food security and environmental impacts (2020): <https://www.eea.europa.eu/themes/agriculture/greening-agricultural-policy/food-security-and-environmental-impacts>. Accessed 18 Apr 2022
2. European Environment Agency: Circular economy in Europe. Developing the Knowledge base. 1st edn. Publications Office of the European Union, Luxembourg: (2016)
3. Dzah, C.S., Duan, Y., Zhang, H., Boateng, N.A.S., Ma, H.: Latest developments in polyphenol recovery and purification from plant by-products: a review. *Trends Food Sci. Technol.* **99**, 375–388 (2020)
4. Gharib-Bibalan, S.: High Value-added products recovery from sugar processing by-products and residuals by green technologies: opportunities, challenges, and prospects. *Food Eng. Rev.* **10**(2), 95–111 (2018)
5. Gullón, P., Gullón, B., Romaní, A., Rocchetti, G., Lorenzo, J.M.: Smart advanced solvents for bioactive compounds recovery from agri-food by-products: a review. *Trends Food Sci. Technol.* **101**, 182–197 (2020)
6. Frutóbidos: Personal communication, Óbidos, Portugal (2021)
7. Bak, I., et al.: Cardioprotective mechanisms of *Prunus cerasus* (sour cherry) seed extract against ischemia-reperfusion-induced damage in isolated rat hearts. *Am. J. Physiol. Heart Circul. Physiol.* **291**(3), H1329–H1336 (2006)
8. Chaovanalikit, A., Wrolstad, R.E.: Total anthocyanins and total phenolics of fresh and processed cherries and their antioxidant properties. *J. Food Sci.* **69**(1), FCT67–FCT72 (2004)
9. Khoo, G.M., Clausen, M.R., Pedersen, B.H., Larsen, E.: Bioactivity and total phenolic content of 34 sour cherry cultivars. *J. Food Compos. Anal.* **24**(6), 772–776 (2011)
10. Piccolella, S., Fiorentino, A., Pacifico, S., D’Abrosca, B., Uzzo, P., Monaco, P.: Antioxidant properties of sour cherries (*Prunus cerasus* L.): role of colorless phytochemicals from the methanolic extract of ripe fruits. *J. Agric. Food Chem.* **56**(6), 1928–1935 (2008)
11. Serra, A.T., Duarte, R.O., Bronze, M.R., Duarte, C.M.: Identification of bioactive response in traditional cherries from Portugal. *Food Chem.* **125**(2), 318–325 (2011)
12. Wojdyło, A., Nowicka, P., Laskowski, P., Oszmianski, J.: Evaluation of sour cherry (*Prunus cerasus* L.) fruits for their polyphenol content, antioxidant properties, and nutritional components. *J. Agric. Food Chem.* **62**(51), 12332–12345 (2014)
13. Liu, Q., Cai, W., Shao, X.: Determination of seven polyphenols in water by high performance liquid chromatography combined with preconcentration. *Talanta* **77**(2), 679–683 (2008)
14. Nowicka, P., Wojdyło, A., Lech, K., Figiel, A.: Chemical composition, antioxidant capacity, and sensory quality of dried sour cherry fruits pre-dehydrated in fruit concentrates. *Food Bioprocess Technol.* **8**(10), 2076–2095 (2015)
15. Seymour, E.M., et al.: Regular tart cherry intake alters abdominal adiposity, adipose gene transcription, and inflammation in obesity-prone rats fed a high fat diet. *J. Med. Food* **12**(5), 935–942 (2009)
16. Siddiq, M., et al.: Characterization of new tart cherry (*Prunus cerasus* L.): selections based on fruit quality, total anthocyanins, and antioxidant capacity. *Int. J. Food Prop.* **14**(2), 471–480 (2011)

17. Piccirillo, C., Demiray, S., Franco, A.R., Castro, P.M.L., Pintado, M.E.: High added-value compounds with antibacterial properties from Ginja cherries by-products. *Waste Biomass Valorizat.* **1**(2), 209–217 (2010)
18. Piccirillo, C., Demiray, S., Ferreira, A.S., Pintado, M.E., Castro, P.M.: Chemical composition and antibacterial properties of stem and leaf extracts from Ginja cherry plant. *Ind. Crops Prod.* **43**, 562–569 (2013)
19. Demiray, S., Piccirillo, C., Rodrigues, C.L., Pintado, M.E., Castro, P.M.L.: Extraction of valuable compounds from Ginja cherry by-products: effect of the solvent and antioxidant properties. *Waste Biomass Valorizat.* **2**(4), 365–371 (2011)
20. Maurício, E., Rosado, C., Duarte, M.P., Fernando, A. L., Díaz-Lanza, A.M.: Evaluation of industrial sour cherry liquor wastes as an ecofriendly source of added value chemical compounds and energy. *Waste Biomass Valorizat.* **11**(1), 201–210 (2020)
21. Yilmaz, F.M., et al.: Sour cherry by-products: compositions, functional properties and recovery potentials—a review. *Crit. Rev. Food Sci. Nutr.* **59**(22), 3549–3563 (2019)
22. AOAC International, G.W. Latimer (ed.): *Official Methods of Analysis of AOAC International*. 20th edn. AOAC International (2016)
23. Neves, M., et al.: Physicochemical and nutritional profile of leaves, flowers, and fruits of the edible halophyte chorão-da-praia (*Carpobrotus edulis*) on Portuguese west shores. *Food Biosci.* **43**, 101288 (2021)
24. Folch, J., Lees, M., Sloane Stanley, G.H.: A simple method for the isolation and purification of total lipids from animal tissues. *J. Biol. Chem.* **226**(1), 497–509 (1957)
25. Fernández, A., Grienke, U., Soler-Vila, A., Guihéneuf, F., Stengel, D B., Tasdemir, D.: Seasonal and geographical variations in the biochemical composition of the blue mussel (*Mytilus edulis* L.) from Ireland. *Food Chem.* **177**, 43–52 (2015)
26. Tvrzická, E., Vecka, M., Staňková, B., Žák, A.: Analysis of fatty acids in plasma lipoproteins by gas chromatography–flame ionization detection: quantitative aspects. *Anal. Chim. Acta* **465**(1–2), 337–350 (2002)
27. Neves, M., Miranda, A., Lemos, M.F., Silva, S., Tecelão, C.: Enhancing oxidative stability of sunflower oil by supplementation with prickled broom (*Pterospartum tridentatum*) ethanolic extract. *J. Food Sci.* **85**(9), 2812–2821 (2020)
28. Konan, K.V., Le Tien, C., Mateescu, M.A.: Electrolysis-induced fast activation of the ABTS reagent for an antioxidant capacity assay. *Anal. Methods* **8**(28), 5638–5644 (2016)
29. Rodrigues, S.S.P., Franchini, B., Graça, P., Almeida, M.D.V.: A new food guide for the Portuguese population: development and technical considerations. *J. Nutr. Educ. Behav.* **38**(3), 189–195 (2006)
30. Górnaś, P., Rudzińska, M., Raczyk, M., Mišina, I., Segliņa, D.: Impact of cultivar on profile and concentration of lipophilic bioactive compounds in kernel oils recovered from sweet cherry (*Prunus avium* L.) by-products. *Plant Foods Hum. Nutr.* **71**(2), 158–164 (2016)
31. Stryjecka, M., Michalak, M., Cymerman, J., Kiełtyka-Dadasiewicz, A.: Comparative assessment of phytochemical compounds and antioxidant properties of kernel oil from eight sour cherry (*Prunus cerasus* L.) Cultivars. *Molecules* **27**(3), 696 (2022)
32. Kang, M.J., Shin, M.S., Park, J.N., Lee, S.S.: The effects of polyunsaturated: saturated fatty acids ratios and peroxidisability index values of dietary fats on serum lipid profiles and hepatic enzyme activities in rats. *Br. J. Nutr.* **94**(4), 526–532 (2005)
33. Mapiye, C., Chimonyo, M., Dzama, K., Hugo, A., Strydom, P.E., Muchenje, V.: Fatty acid composition of beef from Nguni steers supplemented with Acacia karroo leaf-meal. *J. Food Compos. Anal.* **24**(4–5), 523–528 (2011)
34. Attia, Y.A., Al-Harhi, M.A., Korish, M.A., Shiboob, M.M.: Fatty acid and cholesterol profiles, hypocholesterolemic, atherogenic, and thrombogenic indices of broiler meat in the retail market. *Lipids Health Dis.* **16**(1), 1–11 (2017)

35. Fernandes, C.E., da Silva Vasconcelos, M.A., de Almeida Ribeiro, M., Sarubbo, L.A., Andrade, S.A.C., de Melo Filho, A.B.: Nutritional and lipid profiles in marine fish species from Brazil. *Food Chem.* 160, 67–71 (2014)
36. Ghaeni, M., Ghahfarokhi, K.N., Zaheri, L.: Fatty acids profile, atherogenic (IA) and thrombogenic (IT) health lipid indices in *Leiognathusbindus* and *Upeneussulphureus*. *J. Marine Sci. Res. Dev.* 3(4), 1 (2013)
37. Chen, J., Liu, H.: Nutritional indices for assessing fatty acids: a mini-review. *Int. J. Mol. Sci.* 21(16), 5695 (2020)
38. Regulamento (CE) N.o 1924/2006 do Parlamento Europeu e do Conselho de 20 de Dezembro de 2006 relativo às alegações nutricionais e de saúde sobre os alimentos (2006)



Technological Audit as a Strategy to Improve Products and Services Related to Energy Technologies Applied to Buildings

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Abstract. In the context of globalisation, companies must find innovative ways to become more competitive. Continuous assessment of the process of developing and managing new technologies, products and services through *technological audits* is essential for positioning companies in the marketplace. A *technological audit* is a research method that aims to assess the technological capacities, processes and needs of small and medium-sized enterprises. In this study, *the technological audit* conducted within the INNOINVEST project in collaboration with research centres is presented as a method for assessing the technological capacity of enterprises in the field of energy technologies for buildings. The results of the *technological audit* made it possible to identify the areas of improvement in which companies should invest in order to promote operational innovation. In this sense, conducting the *technological audit* proved to be a helpful strategy as it enabled the companies to identify areas of improvement and recommendations for innovation. It should be noted that the auditor must be a specialist with state-of-the-art knowledge in the area of activity to allow a two-way exchange of scientific and technical information with the company.

Keywords: Buildings · Energy · New technologies · Technological audit · Research centres

1 Introduction

The need for timely and continuous review of the effectiveness of risk management and control systems is critical. Businesses are constantly exposed to significant errors, fraud or inefficiencies that can lead to financial loss and increased risk. An evolving regulatory environment, increasing business globalisation, market pressures to improve operations and rapidly changing business conditions result in the need for timely and continuous assurance that controls are operating effectively, and risks are mitigated. The globalisation of markets is forcing companies to take steps to differentiate themselves in

the face of increasing competition in the business world. This differentiation can include increasing the innovative power of companies as a crucial measure to increase their competitiveness [1–3]. The efficient use of resources combined with the capacity for research, development and innovation can favour competitiveness between companies, thus promoting sustainable growth [4–6]. In this way, innovation is one of the keys to the success of companies [2]. Innovation is a process that involves creation, development, and management, leading to new products or tools or to the modernisation and updating of existing processes [5, 7–9]. Constant monitoring of the creation, development and management process through *technological audits* is essential for positioning companies in the market [8, 10, 11].

A *technological audit* is a method of investigation aiming at the evaluation of the technological capacity, procedures, and needs of small and medium-sized enterprises (SME) [10]. The audit is based on a set of indicators that, in addition to the technological base, assess the technological management capabilities of the company, the main vectors of the organisational structures that affect the technological aspect, and the interaction of the company with its environment [10, 12, 13].

The general objective of *technological audits* is to assess the ability of SMEs to integrate new technologies, work with technology partners and better define what they need to successfully integrate these technologies into their business [1, 3, 9].

Specifically, *technological audits* aim to: (i) identify the technologies used by the organisation; (ii) classify these technologies; (iii) identify the weaknesses and strengths of these technologies; (iv) analyse the needs and training potential (e.g. known and unimplemented technologies); and (v) identify the technological potential of the organisation: conditions that need to be met and what technology needs to be implemented to make the organisation more competitive [12–14]. The *technological audit* is conducted by external consultants in close cooperation with the company's management and staff. It is based on the structure: data collection – analysis – synthesis – report [15].

The work presented in this paper is part of the INNOINVEST project [16]. It is a project that involves several public and private entities from Portugal and Spain that are active in the energy products and services for the construction and building sector. The main goal of this project is to foster links between research centres and regional companies in the field of Research, Development, and Innovation (R+D+I) to develop new energy products and services for the construction and building sector [16]. There are three specific objectives associated with the main goal: (i) to provide a permanent structure for cooperation between enterprises and research centres in the Extremadura, Alentejo and Centro Euroregion (EUROACE) area, named *Innoinvest Advisory Programme*; (ii) to increase the number of companies in the EUROACE area developing new innovative energy products and/or services for buildings through R+D+I cooperation with research centres; and (iii) to improve R+D+I cooperation between companies and research centres in the EUROACE area up to the patenting of new products, components and services [16].

Cooperation between research centres and companies is based on three topics: (a) *new materials*, to improve R+D+I on applications of materials with high thermal, acoustic and fire-retardant properties, (b) *cold-heat systems*, by improving R+D+I on applications to create cold-heat systems based on devices that use renewable resources with lower

breakage rates, and (c) *energy storage*, with the aim of improving R+D+I on applications and control systems to create electrical energy storage systems or passive energy storage [16]. These are critical topics for sustainable construction whose main objectives are the optimisation of natural and energy resources.

This study aims to present the *technological audit*, carried out within the scope of the INNOINVEST project, as a methodology to assess the technological capacity of companies and improve products and services related to energy technologies applied to buildings.

2 Methods

The *technological audit* was conducted in four phases: (i) *preparation for the technological audit*: here the auditor collected information from the companies, the status of technologies used in the industry and potential innovations; (ii) *conducting the audit*: as a tool for conducting the audit, an online questionnaire was created in Portuguese to help identify the technologies used in the company and assess their level of implementation; (iii) *analysis of the results*: taking into account the information obtained in the previous two phases, the results were analysed to assess the technological positioning of the company; (iv) *elaboration of the “Plano Innoempresa”*: the auditor prepared an analysis report and a diagnosis of the company, which included the results of the audit, the conclusions that made it possible to determine the technological situation of the company and the action plan for improvement.

The *technological audit* was carried out in several companies in the construction and building sector in EUROACE. This study focused on the seventeen technological audits carried out within the sphere of influence of the Guarda Polytechnic Institute. The Polytechnic of Guarda is a higher education institution for training and education. Through its research unit, it intends to stimulate research and development in Beira Interior region of Portugal.

To perform the *technological audit*, the questionnaire developed within the INNOINVEST project was used to identify the technologies used in the company and to assess the degree of implementation of these technologies. The questionnaire covers the following topics: (i) general company data; (ii) human resources; (iii) the main products/services of the company; (iv) identification of processes and technologies; (v) classification of technologies; (vi) key factors for innovation; (vii) innovation opportunities; (viii) identification of the potential for the application of new technologies and (ix) classification of new technologies. In describing the previous topics in more detail, it should be noted that in topics (i) and (ii) general information about the company was collected and the organisational structure of the company was briefly described. Topic (iii) described the three main product/service lines. In topic (iv), the auditor identified the company's technologies, both those used in the production process and other tasks necessary for the development of the company's activity. In topic (v), the auditor, in collaboration with the entrepreneur, identified the leading technologies used by the company and classified them according to competitive impact, the competitive advantage that the technology represents for the company, the level of maturity, the stage of development that the technology is in and the importance of these technologies for the company, the impact of the technology on the company's various products and services (Table 1).

It should be noted that an external auditor conducted the *technological audit* because, since most companies are small or even micro-enterprises, their human resources tend to focus on technologies they regularly use rather than on new technologies. Add to this fact the limited availability of human resources to analyse and implement audit requests. The research centres supported the conducting of the *technological audits*.

Table 1. Classification of technology according to the competitive impact, the level of maturity and the importance of technology for the company

Competitive Impact	Emerging - Technology with high potential to change the competitive basis of activity
	Key - Critical technology for success as it maintains the competitive position of the enterprise
	Base - Essential technologies that must be present in the sector in which the company operates but do not provide a competitive advantage
Level of Maturity	Emerging - Technology that is not yet on the market or is at a very early stage
	Growing - Technology that is present in the products/processes of leading companies, whose use is beginning to become generalised and may develop further in the future
	Mature - A technology that is known and present in the vast majority of companies and for which no significant advances are expected in the future
	In decline - Technologies that are being abandoned by companies
Importance of the Technology	Very High - Significantly affects all products and services of the company
	High - Most of the company's products are affected
	Average - It only affects a number of relevant products
	Low - It only affects a number of products/services that are not relevant to the company

For topic (vi), the assessor needs to analyse certain factors that affect the company's innovation management, i.e. aspects of the organisation related to the company's culture of innovation, how new products and services are identified and customers' needs are anticipated, or how the company encourages employees to bring in ideas and creativity, etc.

Topic (vii) is about identifying the activities within the organisation where innovation needs, and opportunities, can be detected. The opportunities that the auditor seeks to detect may be based on product and service innovation, process, management and technological innovation through the incorporation of technologies that enable the efficient and successful introduction of new products into the market.

Topic (viii) aims to identify the possibility of innovation in some technologies that are the subject of the project: new materials with high thermal, acoustic and fire-retardant properties, cold-heat systems and energy storage. In point (ix), the most interesting technology selected previously is evaluated according to the following parameters: (a) *impact on competitive position*, i.e. how will the technology improve the competitive position in play, using the classification terms low, medium or high, (b) *potential market*, using the classification terms, technology not in demand (potential customers do not recognise the benefits of the new technology) or technology in demand (high demand and acceptance by customers), and (c) *degree of knowledge the company has about the technology*, using the classification terms low, medium, high and very high. It should be noted that the classification scales have been converted into numerical values to facilitate the completion of the questionnaire.

In the next section the result of the *technological audit* and the *Action Plan* of one of the companies involved in the INNOINVEST project will be presented.

3 Results

Of the companies that participated in the *technological audit*, construction is the most represented activity sector, followed by manufacturing (Fig. 1).

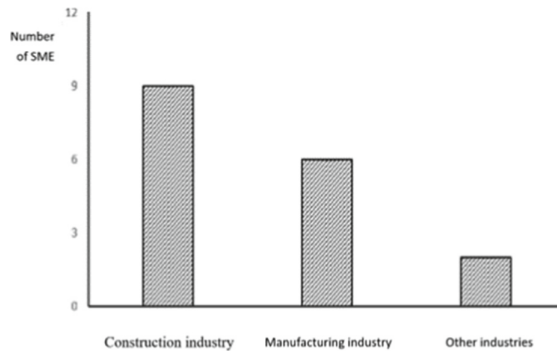


Fig. 1. SME enterprises by sector of activity

The main activities of the audited companies are aluminium window frames and aluminium processing (Fig. 2).

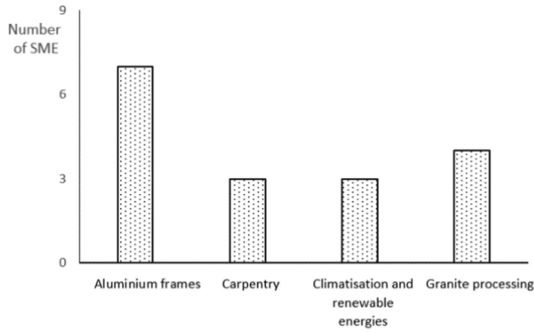
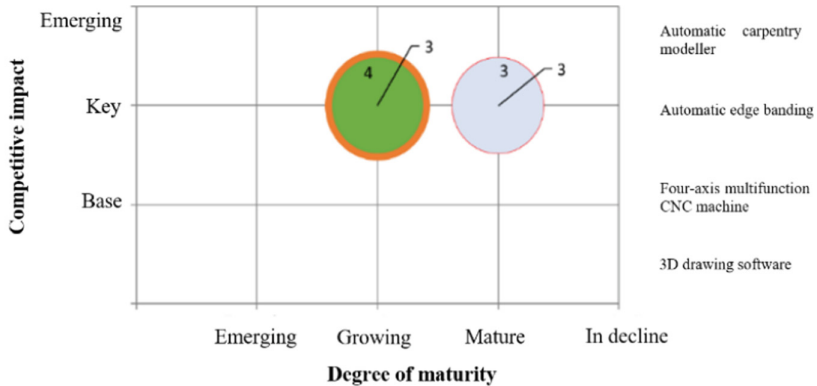


Fig. 2. SME enterprises by activity

3.1 Technological Audit

After all the information had been obtained in the previous steps, the results were analysed to assess the technological positioning of the companies. For this purpose, the matrix of technological differentiation, a radar chart of key factors for innovation and a matrix of technological impact were created.

Using the matrix for technological differentiation (Fig. 3), it is possible to check that all the technologies identified by the auditor and entrepreneur have a competitive effect that is classified as **Key**. As far as the maturity of the technologies is concerned, the *technological audit* revealed that the 3D drawing software and the *four-axis multifunction CNC machine* have a degree of maturity level that is classified as **Growing**, while the *automatic carpentry modeller* and *automatic edge banding* are classified as **Mature**.



The numeric label corresponds to the degree of importance of the technology

Fig. 3. Matrix of technological differentiation

Regarding the key factors for innovation, the radar chart (Fig. 4) shows that the most important key factor for companies is innovation in business planning (numeric value

= 3), while cooperation has the lowest value (numeric value = 0). This last result could indicate a lack of inclination to carry out projects and business in cooperation with other companies, such as research centres.

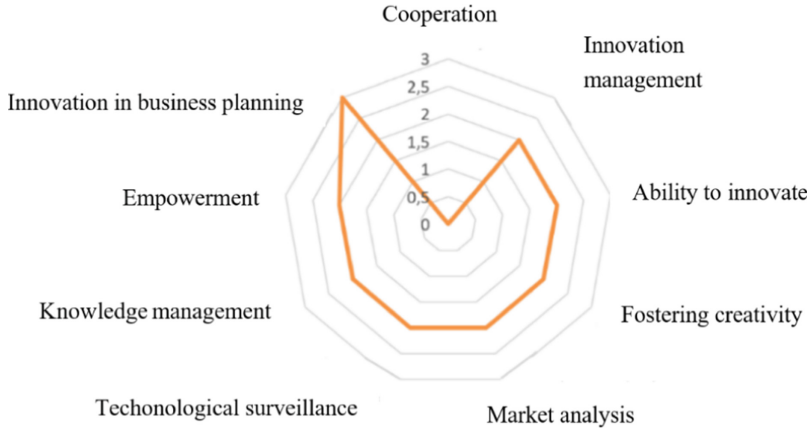
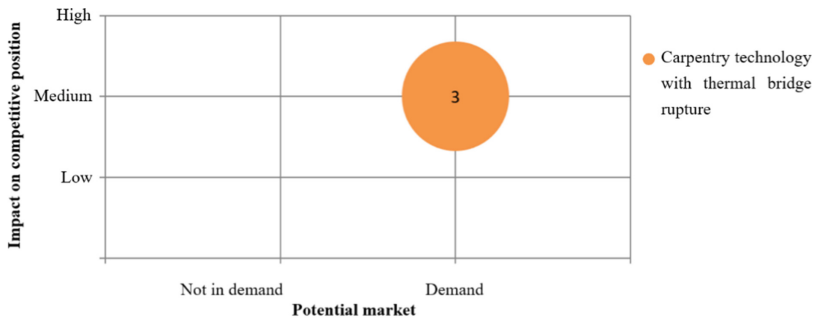


Fig. 4. Radar chart of the key factors for innovation.

Regarding technological impact, the classification of new technologies was made, considering the parameters *impact on competitive position*, *potential market*, and *degree of knowledge the company has about the technology*. Figure 5 shows the technological matrix for **carpentry technology with thermal bridge rupture**. The results indicate that it is a technology in demand and that it has an average impact on the company’s competitive position in the market. On the other hand, it shows that the company’s knowledge about the technology is average. This result shows that this technology can increase the competitiveness of the company insofar as it is demanded by the market, for which it is necessary to deepen its technical and scientific knowledge.



The numeric label corresponds to the degree of importance of the technology

Fig. 5. Matrix of technological impact

3.2 Action Plan

The term *audit* has a negative connotation in the business world because it is associated with inspection. The development of the *Action Plan* made it possible to mitigate companies' resistance to participating in the *technological audit*. An *Action Plan* named the "*Plano Innoempresa*" was produced. This was a document to analyse, diagnose and evaluate the technological capacity of the company, identify weaknesses and propose improvements and ways to move from the current technological situation to the desired technological situation. A work plan was also drawn up, identifying actions to develop or improve products and services related to technologies associated with the INNOINVEST project, such as new materials with high thermal, acoustic and fire-retardant properties, cold-heat systems and energy storage systems. In this way, the carpentry company received indications that the company needs to master all key technologies, maintain support for essential technologies and be aware of at least one of the emerging technologies in order to be prepared for possible technological changes in the future. Recommendations were also made, such as raising funds to invest in new technologies, implementing computer systems to support commercial, operational and financial management, developing web solutions to support online business, and finding partners (e.g. research centres) to develop new products.

4 Conclusion

In the context of the current scenario, technological innovation reinforces the need for a continuous process of improvement. Adapting to this globalised reality allows technologies to be implemented and quickly assimilated by professionals to create benefits that become competitive advantages. Conducting the *technological audit* proved to be a helpful strategy as it allowed companies to identify areas for improvement and recommendations for innovation.

Many of the companies interviewed were small and micro enterprises with family roots, without market studies and focused on regional market niches. In the face of the economic crisis triggered by the Coronavirus 2019 disease, however, despite being receptive to the proposals presented, the companies were only concerned about their survival, so the implementation of the improvement proposals, which always require costs in the form of personnel, materials or both, was not considered feasible. It is stressed that the auditor must be an expert who knows the state of the art in his field of activity in order to allow a two-way exchange of scientific and technical information with company managers.

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References

1. de Vasconcelos, R.B.B., dos Santos, J.F., de Andrade, J.A.: Inovação em Micro e Pequenas Empresas: Recursos e Capacidades. *Rev. Adm. Contemp.* **25**, (2021)
2. Fuck, M.P., Vilha, A.M.: Inovação Tecnológica: da definição à ação. *Contemporâneos. Revista de Artes e Humanidades.* 21 (2012)
3. Cooper, R.G., Edgett, S.J.: Maximizing productivity in product innovation. *Res. Technol. Manag.* **51**, 47–58 (2008). <https://doi.org/10.1080/08956308.2008.11657495>
4. Marques, G., Pitarma, R.: Enabling smart homes through health informatics and Internet of Things for enhanced living environments. In: Rocha, Á., Adeli, H., Reis, L.P., Costanzo, S., Orovic, I., Moreira, F. (eds.) *Trends and Innovations in Information Systems and Technologies. Advances in Intelligent Systems and Computing*, vol. 1161, pp. 76–85. Springer, Cham (2020). https://doi.org/10.1007/978-3-030-45697-9_8
5. Marques, G., Pitarma, R.: Indoor air quality monitoring for enhanced healthy buildings. In: Abdul Mujeebu, M. (ed.) *Indoor Environmental Quality*. IntechOpen, London (2019)
6. Marques, G., Pitarma, R., Garcia, N.M., Pombo, N.: Internet of Things architectures, technologies, applications, challenges, and future directions for enhanced living environments and healthcare systems: a review. *Electronics* **8**, 1081 (2019). <https://doi.org/10.3390/electronics8101081>
7. O'Donnell, J.B.: Innovations in audit technology: a model of continuous audit adoption. *J. Appl. Bus. Econ.* **10**, 11–20 (2010)
8. Kosenko, O., Cherepanova, V., Dolyna, I., Matrosova, V., Kolotiuk, O.: Evaluation of innovative technology market potential on the basis of technology audit. *Innovative Mark.* **15**, 30–41 (2019). [https://doi.org/10.21511/im.15\(2\).2019.03](https://doi.org/10.21511/im.15(2).2019.03)
9. van Beers, C., Zand, F.: R&D cooperation, partner diversity, and innovation performance: an empirical analysis. *J. Prod. Innov. Manag.* **31**, 292–312 (2014). <https://doi.org/10.1111/jpim.12096>
10. Lois, P., Drogalas, G., Karagiorgos, A., Tsikalakis, K.: Internal audits in the digital era: opportunities risks and challenges. *EuroMed. J. Bus.* **15**, 205–217 (2020). <https://doi.org/10.1108/EMJB-07-2019-0097>
11. Engel, V., Deponti, C.M.: Inovação Tecnológica, Institucionalismo Econômico e Path Dependence: Uma proposta Teórico- Metodológica para Análise de Políticas de Inovação. *Stud. Soc. Sci. Rev.* **2**, 330–346 (2021). <https://doi.org/10.54018/sssrv2n3-015>
12. Gomes, E., Nirazawa, A.N.: Auditorias tecnológica e de inovação: contribuições para Pequenas e Médias empresas. *CGE.* 6, 38–54 (2018). <https://doi.org/10.32888/cge.v6i2.12776>
13. Pizzi, S., Venturelli, A., Variale, M., Macario, G.P.: Assessing the impacts of digital transformation on internal auditing: a bibliometric analysis. *Technol. Soc.* **67**, 101738 (2021)
14. Hassan, N.A., Zailani, S.H.M., Abu Hasan, H.: A meta-analysis of integrated internal audit management effectiveness towards business sustainability. *Pertanika J. Soc. Sci. Humanit.* **29**, 233–252 (2021). <https://doi.org/10.47836/pjssh.29.S2.16>
15. Yakimova, V.A.: Opportunities and prospects for using digital technologies in auditing. *Vestn. St. Petersburg Univ. -Ekon.* **36**, 287–318 (2020). <https://doi.org/10.21638/spbu05.2020.206>
16. PROYECTO INNOINVEST – Promoção da I + D + I em produtos e serviços energéticos relacionados com a construção, <http://innoinvestproject.eu/pt/home-2/>



Binary and Ternary Mixtures for SI Engines: A Review

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Abstract. This work aims to review the contribution of biofuels as complement or alternative to gasoline in spark ignition (SI) engines, taking into account the chemical nature and properties of these renewable fuels and describing their effects on engine performance and exhaust emissions. The limits imposed by the legislation, regarding the use of first-generation biofuels, as well as the maturity and economic viability of the production of drop-in-fuels are also fundamental drivers for the technological solutions that will be adopted in the next decades to promote sustainable mobility using SI engines.

Keywords: Alternative fuel · Biofuel · Binary and ternary blend · SI engine

1 Introduction

Internal combustion engines have been optimized to use fossil fuels and fuel additives have been proposed to increase fuel performance and minimize emissions.

One of the strategies to improve the thermal efficiency of SI engines is to increase their compression ratio but an engine with a high compression ratio requires a fuel with a high octane index (OI) [1]. In the 1920s, tetraethyl lead was added to gasoline in order to increase the fuel OI but the growing detection of lead in air, water, soils and plants rapidly raised concerns with lead toxicity and the environmental impacts of this option [2]. Therefore, in the 1970s, lead compounds would be replaced by methyl tertiary butyl ether (MTBE) an organic ether with good miscibility with gasoline. With the advent of the promotion of renewable fuels, bioethanol was used as an additive to gasoline with similar advantages for OI and exhaust emissions [3].

As most renewable fuels are not completely equivalent to fossil fuels, their use has been gradually implemented as fuel additives in moderate percentages in order to minimize negative effects on engine behaviour. Advanced biofuels, which are currently being developed, can overcome these limitations, achieving true equivalence to fossil fuels and, therefore, can be used without restrictions in unmodified engines.

The purpose of this work is to review the literature on liquid biofuels proposed as additives or alternative fuels to gasoline. Liquid fuels are easier to store and transport

than gaseous fuels, but in order to burn they must be transformed into a gas or quasi-gas. The effects of these biofuels on engine performance will be discussed as well as their potential to influence emissions.

2 Current Status of Liquid Biofuels

Regardless of the type of engine used, there are five types of liquid biofuels that are currently available in industrial quantities and have been regularly integrated in the composition of commercial fuels. Table 1 identifies these biofuels, as well as the raw materials and processes that gave rise to them.

Table 1. Identification of commercially available liquid biofuels [4–7].

Raw material	Conversion process	Liquid biofuel	Type
Sugar (sugar cane)	Fermentation, distillation	Bioethanol	Alcohol
Starch (corn)	Hydrolysis, fermentation, distillation		
Bioethanol (47%) and isobutene (53%)	Chemical reaction	Bio-ETBE (*)	Ether
Oilseeds	Pressure, extraction	Vegetable oil	Lipids
Vegetable oil, animal fat, residual oil	Transesterification	Biodiesel	Ester
	Catalytic hydrotreatment	Hydrogenated vegetable oil (HVO)	Alkanes

(*) In the production of bio-ETBE, a significant percentage of fossil fuels is used.

The two biofuels available in greater quantities are bioethanol and biodiesel because they are produced from existing crops using mature technologies [3].

The bioethanol industries are based on corn and sugar cane, but in the last decades production of cellulosic ethanol has been developed to reduce wastes and answer the increasing limitations on the use of first generation fuels [3, 8].

Bio-ETBE is listed as a biofuel since it can be produced from bioethanol therefore it is partially of renewable origin [5].

The kinematic viscosity of vegetable oils and animal fats is 5 to 10 times higher than that of diesel, which limits their application in conventional compression ignition engines [9]. The viscosity of biodiesel, obtained by transesterification of vegetable oils, shows a significant improvement compared to pure vegetable oil [10]. The influence of the feedstock in the biodiesel properties and the requirements of the transesterification process have limited the raw materials used for biodiesel production to essentially pure vegetable oils. The catalytic thermochemical conversion of lipids to bio-oils allowed the use of a wider range of lipid materials even those partially degraded or with some percentage of contaminants enabling the valorisation of waste materials [11, 12].

The catalytic hydrodeoxygenation of lipids occurs at temperatures higher than 400 °C, in a hydrogen-rich atmosphere and produces HVOs that are bio-oils rich in

aliphatic hydrocarbons [13]. HVOs are distilled to yield different biofuel fractions with characteristics adequate for replacement of various fossil fuels [14–16].

Table 2 gives a general view of fuel formulations containing biofuels that are used in different regions.

Table 2. Different formulations of commercial fuels containing biofuels [4, 6, 7, 9, 10, 13, 17–20].

Fuel	Markets and applications
Methanol (M)	Gasolines supplemented by methanol or 100% methanol are commercialized in China; depending on the region, fuel mixtures range from M5 to M100 with M15 being the national standard
Ethanol (E)	In Brazil, Paraguay, Sweden and USA are sold gasolines supplemented with bioethanol up to 85%. E25 is the standard blend in Paraguay and Brazil. The EN 228 standard establishes the maximum limit of 10% vol. of bioethanol for gasoline marketed in Europe
MTBE, ETBE	MTBE and ETBE are used as gasoline additives at concentrations typically lower than 20%
Vegetable oil (VO)	VO is marketed as biofuel mainly in Germany. VO can be used pure in adapted engines. Alternatively, VO can be used mixed with diesel
Biodiesel (B)	Biodiesel can be used pure or mixed with diesel up to B20. The EN590 standard establishes the maximum limit of 7% vol. of FAME for diesel sold in Europe
HVO	HVO can be used pure (requires recalibration of injection systems) or mixed with diesel

3 Alternative Fuels for SI Engines

Other alternative fuels produced by biological or thermochemical processes are being proposed for gasoline partial or complete replacement in engines. Some of them may be designated as biofuels as they are obtained from biomass while others are renewable fuels with low carbon footprint, since they are produced from polymeric wastes. Table 3 shows some of these alternative fuels.

Butanol has some advantages over ethanol: higher energy content (33.1 MJ.kg^{-1} against 26.8 MJ.kg^{-1} of ethanol), less corrosion issues due to the presence of water, lower vapor pressure [22]. Butanol also has molecular weight and physical and chemical properties more similar to gasoline than those of ethanol.

Biobutanol can be produced from lignocellulosic biomass through advanced fermentation processes, ABE (acetone-butanol-ethanol) or IBE (isopropanol-butanol-ethanol), using bacteria of the clostridium genus [21, 28]. Separating butanol from the other components in ABE or IBE mixtures is very expensive. Therefore, there is an interest in studying these mixtures of ABE or IBE as a potential fuels for direct use in SI engines [22]. More recently, the fermentation of sugars with genetically modified organisms

Table 3. Alternative fuels for SI engines.

Raw material	Conversion process	Fuel	Functional groups	Ref.
Biomass	ABE or IBE fermentation	ABE, IBE	Mixture of alcohols and ketone	[21, 22]
Biomass	Fermentation	Biobutanol	Alcohol	[21]
By-product of alcoholic fermentation	Distillation	Fusel oil (C ₅ H ₁₁ OH)	Alcohol	[23]
Tire	Pyrolysis	Tire bio-oil (TPO)		[24]
Plastic waste: PS, PP, LPE, HDPE	Pyrolysis	Plastic bio-oil (PPO)	Alkanes	[25]
	Pyrolysis, distillation	Plastic bio-oil distillate (DPPO)		[26]
Hard resin of yang	Pyrolysis, distillation	Gasoline-like fuel (GLF)		[27]

able to convert them to butanol or isobutanol has been developed by companies such as BUTMAX [29] or GEVO [30] creating an availability of this fuel at commercial scale. Considering the properties of isobutanol and the ease of converting ethanol production units to the production of isobutanol, it is expected that this biofuel will become a hegemonic option for replacing gasoline.

Fusel oil is the least volatile fraction of the ethanol distillation process and contains some residual ethanol and other alcohols with higher molecular weight, such as isoamyl and isobutyl that are co-produced during the fermentation process. The proportions of the alcohols in fusel oil depend on the raw materials used as source of fermentable sugars, microorganisms and operational conditions [23].

Polymeric waste materials may be converted to hydrocarbon-rich bio-oils through thermal and catalytic pyrolysis [31]. Pyrolysis bio-oils, obtained from various plastic wastes, were distilled to isolate their lighter components and yielded liquid fractions with similarities to gasoline, which may be used as a renewable and low carbon footprint fuel since they are produced from wastes [32].

Yang's resin is a mixture of simple and complex terpenes extracted, by the traditional process of resin production, from the tree with the same name. The pyrolysis of Yang's resin reduces its viscosity decomposing its high molecular weight components to yield a light bio-oil with energy content comparable to gasoline [27].

The performance of alternative fuels proposed for SI engines and the associated exhaust emissions were evaluated by different authors using: pure fuels, binary mixtures with gasoline and ternary mixtures of two biofuels and gasoline. This review will not include mixtures containing methanol, MTBE and ethanol because they have been reviewed in previous works [33]. Table 4 reviews the behaviour of alternative fuels tested pure in SI engines.

Table 4. Alternative fuels tested pure in SI engines.

Fuels tested	Effect of fuel on engine performance	Effect of fuel on exhaust gas emissions	Ref.
Fusel oil (F)	General decline in torque and brake thermic efficiency (BTE). Increase in brake specific fuel consumption (BSFC)	CO and UHC emissions increased 21 and 25% respectively. NO _x decreased by 31%	[23]
Pyrolysis bio-oils distillates from plastic waste (DPPO)	Comparable engine performance and reduction of fuel consumption for all DPPO (PS, PP, LPE, HDPE)	All distillates except PS bio-oil distillate produced more CO. All distillates, except PP bio-oil distillate, produced more NO _x	[32]
Pyrolysis bio-oils distillates from hard resin of yang (GLF)	GLF showed better results than gasoline for torque, BTE and BSFC	GLF had lower emissions of CO and UHC and higher emissions of NO _x	[27]

DPPO have the particularity of being produced from fossil waste, therefore, the energy recovery of these wastes for the production of fuels is a more sustainable solution than landfilling deposition or incineration.

Other alternative fuels for SI engines were tested in the form of binary mixtures with gasoline (Table 5).

The results presented in Tables 4 and 5 indicate that alcohols continue to be the most tested biofuels for gasoline replacement in SI engine tests. There is a growing interest in the use of C3 or C4 alcohols such as propanol, isopropanol, butanol or isobutanol due to their higher energy content, lower hygroscopicity and similar properties to gasoline [34, 35, 38–41, 43, 44]. As their production from renewable sources is achieving a higher degree of technological maturity, the choice of C3 or C4 alcohols for SI engines requires validation to define maximum incorporation rates, need of engine adaptations, associated emissions, among other data that support transition to their use at commercial scale. Using mixtures of alcohols with gasoline usually resulted in a decrease of CO and UHC emissions due to a higher oxygen-to-fuel ratio that favors complete oxidation of the fuel components but also caused an increase in NO_x emissions. Alcohols also produce greater volume of combustion products than gasoline (called the “alcohol bonus”) leading to greater expansion work resulting in higher overall engine efficiency than expected [1].

The performance and emissions of SI engines fed with mixtures of C3 or C4 alcohols and gasoline were comparable to those of gasoline or even showing slight improvements, what suggests that these blends are suitable for use in unmodified SI engines [35, 43, 44]. Nevertheless, some differences in the data obtained by different authors that tested mixtures of gasoline with butanol or isobutanol, suggest that further tests should be made to clearly define the effects of such biofuels in engine behaviour and exhaust emissions [38, 39].

Table 5. Alternative fuels tested in the form of binary mixtures with gasoline and compared with pure gasoline, in SI engines operated in equivalent conditions.

Binary mixtures tested	Effect on engine performance	Effect on exhaust gas emissions	Ref.
Gasoline + isopropanol (iP) <i>iP10 to iP30 blends</i>	iP increased the pressure in the cylinder, the rate of heat release and BTE	iP increased NO _x emissions and decreased CO and UHC emissions	[34]
Gasoline + propanol (P) <i>P5 to P20 blends</i>	P15 stood out among the mixtures tested, with torque up to 3.6% and BSFC up to 2.8%	Propanol blends reduced CO and UHC emissions by 10.9 and 14.2% respectively and increased NO _x emissions	[35]
Gasoline + IBE + W (water) <i>IBE9W1 blend</i>	The blend IBE9W1 had higher BTE than 100% gasoline	The blend IBE9W1 had lower emissions of CO, NO _x and BTX (benzene, toluene and xylene) but higher UHC emissions	[22]
Gasoline + acetone (A)	A10 blend improved power gains (5.2%), torque (2.1%) and volumetric efficiency (3.2%) relatively to 100% gasoline	A10 blend reduced CO emissions by 43% and UHC by 33% relatively to 100% gasoline	[36]
Gasoline + ABE <i>ABE30(6:3:1), ABE30(3:6:1) blends</i>		ABE30(6:3:1) blend reduced emissions of UHC, CO, benzene and 1,3-butadiene ABE30(3:6:1) blend reduced emissions of xylenes	[37]
Gasoline + ABE + W (water) <i>ABE29W1 blend</i>	ABE29W1 blend increased engine torque (3.1–8.2%) in comparison with gasoline	ABE29W1 blend reduced CO (9.8–35.1%), UHC (27.4–78.2%) and NO _x (4.1–39.4%) emissions relatively to gasoline	[21]
Gasoline + isobutanol (iB) <i>iB5 to iB15 blends</i>	Isobutanol blends had lower cylinder pressure and lower heat release rate than gasoline	Isobutanol blends decreased emissions of CO, UHC and NO _x by 7.1, 13.7 and 19.8% respectively relatively to gasoline	[38]

(continued)

Table 5. (continued)

Binary mixtures tested	Effect on engine performance	Effect on exhaust gas emissions	Ref.
Gasoline + n-butanol (B) <i>B10 to B30 blends</i>	Butanol blends increased maximum pressure in the cylinder proportionally to its content in the fuel blend	Butanol blends had lower CO and UHC emissions but higher NO _x emissions than gasoline	[39]
Gasoline + n-butanol (B) <i>B20 and B40 blends</i>	Butanol blends decreased torque and BTE and increased BSFC	Butanol blends had slightly lower emissions for UHC and NO _x	[40, 41]
Gasoline + fusel oil (F) <i>F10 to F30 blends</i>	F30 blend had the highest increase in torque (3.4%) and BSFC (+7.7%)	Fusel oil blends had lower NO _x emissions and higher UHC and CO emissions	[42]
Gasoline + fusel oil without water (F) <i>F50 blend</i>	F50 blend had lower torque and BTE and higher BSFC than gasoline	CO and UHC emissions increased and NO _x decreased in relation at gasoline	[23]
Gasoline + tires pyrolysis bio-oil (TPO) <i>TPO10 to TPO100 blends</i>	TPO blends up to 60% did not degrade engine performance	TPO blends up to 60% did not increase CO, UHC and NO _x emissions. Desulfurization of TPO is advised	[24]
Gasoline + plastics pyrolysis bio-oil (PPO) <i>PPO15 blend</i>	PPO15 blend decreased BSFC and BTE by 4.1 and 9.4% respectively	PPO15 blend decreased CO emissions by 9.7% and increased UHC and NO _x emissions by 52.6 and 24.2% respectively	[25]
Gasoline + plastics pyrolysis bio-oil distillate (DPPO) <i>DPPO10 to DPPO50 blends</i>	DPPO50 blend increased engine BTE by 19% and decreased BSFC by 26.8%	DPPO blends increased CO and NO _x emissions by 70 and 60% respectively and UHC decreased by 43.6% in relation at gasoline	[26]

The intermediate fermentation products ABE and IBE that incorporate some water content showed a good potential be used as alternative fuels, due to their good performance and low emissions [21]. Dehydration to eliminate water or further distillation steps to isolate butanol from the ABE and IBE mixtures is therefore unnecessary. Mixtures of gasoline with ABE also reduced unregulated engine emissions.

The presence of water in fusel oil negatively affected engine performance and emissions [45]. To avoid this negative effects, fusel oil should be dehydrated and ignition must be optimized to the fuel characteristics [23].

The plastics pyrolysis bio-oil (PPO), like other pyrolysis bio-oils, contains heavier compounds that are more difficult to evaporate and burn, causing inefficient combustion.

Distillation of PPO allows to separate this heavier organic fraction and solid residues from the light organic fraction with much better fuel properties [26]. The only drawback of the DPPO is the increment of NO_x emissions as observed for all oxygenated fuels.

Since the replacement of gasoline by a single biofuel or biofuel type may improve some aspects of fuel performance and exhaust emissions but negatively affect others, the use of ternary mixtures of gasoline and two different biofuels has been tested by different authors with the purpose of achieving optimal combustion conditions by combining fuels with different chemical composition and properties (Table 6).

Table 6. Alternative fuels incorporated in ternary mixtures with gasoline in SI engines.

Ternary mixtures tested	Effect on engine performance	Effect on exhaust gas emissions	Ref.
Gasoline + methanol (M) + fusel oil (F) without water <i>M15F1, M15F3 blends</i>	The characteristic curves (torque, BSFC, BTE) produced by mixtures M15F1 and M15F3 were comparable to those of gasoline	CO, UHC and NO_x emissions of the M15F1 and M15F3 blends were identical to those of gasoline	[46]
Gasoline (G) + ethanol (E) + methanol (M) <i>GEM blends</i>	GEM has the same stoichiometric air-fuel ratio as the E85 (9.7: 1) and can be used as an alternative to E85 that has limitations on cold starting		[47]
Gasoline + plastic pyrolysis bio-oil (PPO) + ethanol (E) <i>PPO15E5 blend</i>	PPO15E5 blend caused a 7.2% increase of BSFC and a 0.4% decrease of BTE relatively to gasoline	PPO15E5 blend had lower CO and NO_x emissions (24.1% and 0.4%, respectively) and 28.5% higher UHC emissions relatively to gasoline	[25]

The addition of dehydrated fusel oil to a gasoline-methanol mixture allowed to explore the co-solvent function of fusel oil whose physical-chemical properties are intermediate between gasoline and methanol.

In some markets, is available a mixture of three fuels: gasoline, ethanol and methanol (GEM), in which ethanol is added as a co-solvent for gasoline and methanol. GEM has the same stoichiometric air/fuel ratio ($\text{AFR} = 9.7:1$) as the E85 but it has some advantages namely the ease of cold starting [47]. The high volatility and low viscosity of methanol may have advantages regarding the behavior of fuel mixing in the engine, but this alcohol also presents significant differences from gasoline, that is, high polarity and hygroscopicity that can lead to incomplete mixing of binary mixtures. Higher alcohols can be added as stabilizing agents to improve fuel homogeneity and ethanol or propanol are the best candidates as butanol or other alcohols with higher molecular weight are too different from methanol to efficiently play the role of co-solvent [48].

With the addition of ethanol to the mixture of gasoline + bio-oil from plastic pyrolysis (PPO), engine performance was improved and NO_x emissions were marginally controlled. Gasoline and PPO are perfectly miscible, but the higher density and viscosity of PPO had a negative impact on engine performance. The addition of ethanol not only attenuated the aforementioned properties but also increased the local availability of oxygen, improving combustion efficiency [25].

4 Conclusions

Biofuels have differences, in chemical structure and composition, in relation to the reference fossil fuels that directly affect their engine performance and exhaust emissions.

The partial or complete replacement of gasoline by renewable alcohols and ethers improves the fuel OI and reduces CO and UHC emissions. These reductions in CO and UHC are transversal to all biofuels, due to the presence of oxygen in their composition a characteristic that improves local availability of this oxidant element therefore leading to a more complete combustion of the fuel components.

Fuels derived from plastic waste and tires are more similar to gasoline than alcohol biofuels, thus they could be used pure or with higher incorporation rates in the SI engines. Inefficient combustion and increase of NO_x emissions maybe negative impacts of the use of these biofuels, suggesting that their integration in ternary blends may contribute to optimize their performance.

The behaviour of pure GLF outperformed gasoline in terms of engine behaviour (higher torque and thermal efficiency and lower specific consumption) and exhaust gas emissions (lower CO and UHC) although increasing NO_x emissions.

Propanol, IBE, acetone, ABE, butanol, fusel oil and distillates from tire, plastic and resin pyrolysis bio-oils are alternative renewable fuels that show a high potential to effectively replace gasoline, totally or partially, in the form of binary or ternary blends in order to promote a more sustainable use of SI engines.

References

1. Martins, J.: Motores de Combustão Interna. (Engebook, 2020)
2. Needleman, H., Gee, D.: 3 Lead in petrol 'makes the mind give way'. *Lessons from Heal. hazards* 46–75 (2005)
3. Bušić, A., et al.: Bioethanol production from renewable raw materials and its separation and purification: a review. *Food Technol. Biotechnol.* **56**, 289–311 (2018)
4. IEA-ETSAP. Production of Liquid Biofuels: Technology Brief. 1–26 (2013).<https://doi.org/10.1111/j.1745-4514.2010.00447.x>
5. Rutz, D., Janssen, R.: *Biofuel Technology Handbook*. WIP Renewable Energies (WIP Renewable Energies, 2008)
6. IEA. Technology Roadmap - Biofuels for Transport. [papers2://publication/uuid/7E683CA3-E72A-439B-8C06-CDAADB021565](https://publication/uuid/7E683CA3-E72A-439B-8C06-CDAADB021565) (2011).<https://doi.org/10.1787/9789264118461-en>
7. IEA-AMF. Advanced Motor Fuels. [https://www.iea-amf.org/content/fuel_information/fuel_info_home\(2020\)](https://www.iea-amf.org/content/fuel_information/fuel_info_home(2020))
8. Taherzadeh, M.J., Karimi, K.: Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. *BioResources* **2**(3), 472–499 (2007)

9. Elsbett, G., Bialkowski, M.: Engines running on pure vegetable oil as regrowing fuel - History, Development, Experience, Chances (2003)
10. EurObserv'ER. Biofuels Barometer. Syst. Solaires **210**, 3–30 (2012)
11. Ben Hassen-Trabelsi, A., Kraiem, T., Naoui, S., Belayouni, H.: Pyrolysis of waste animal fats in a fixed-bed reactor: production and characterization of bio-oil and bio-char. Waste Manag. **34**, 210–218 (2014).
12. Taufiqurrahmi, N., Bhatia, S.: Catalytic cracking of edible and non-edible oils for the production of biofuels. Energy Environ. Sci. **4**, 1087 (2011)
13. Huber, G.W., O'Connor, P., Corma, A.: Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. Appl. Catal. A Gen. **329**, 120–129 (2007)
14. Aatola, H., Larmi, M., Sarjovaara, T. & Mikkonen, S. Hydrotreated Vegetable Oil (HVO) as a Renewable Diesel Fuel: Trade-off between NO_x, Particulate Emission, and Fuel Consumption of a Heavy Duty Engine. SAE Technical Paper 2008–01–2500. SAE Tech. pp. 12 (2008). <https://doi.org/10.4271/2008-01-2500>
15. Lehmus, P.: Large scale chemical conversion of oils and residues in Rotterdam. In: European Biofuels Technology Platform - 6th Stakeholder Plenary meeting **26** (Neste Oil, 2014)
16. Galp. Biocombustíveis. <https://www.galp.com/corp/pt/sobre-nos/o-que-fazemos/refinacao-distribuicao/biocombustiveis> (2020)
17. Topgül, T.: The effects of MTBE blends on engine performance and exhaust emissions in a spark ignition engine. Fuel Process. Technol. **138**, 483–489 (2015)
18. Directive 2003/30. Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport THE. Communities 4, 42–46 (2003)
19. DL 89/2008. Especificações técnicas dos combustíveis. Diário da República, 1.^a série — N^o 104 — 30 de Maio de 2008 (2008)
20. Kalnes, T.N., Marker, T., Shonnard, D.R., Koers, K.P.: Green diesel production by hydrotreating renewable feedstocks. Biofuels Technol. **4**, 7–11 (2008)
21. Li, Y., et al.: Effect of water-containing acetone-butanol-ethanol gasoline blends on combustion, performance, and emissions characteristics of a spark-ignition engine. Energy Convers. Manag. **117**, 21–30 (2016)
22. Li, Y., Chen, Y., Wu, G., Liu, J.: Experimental evaluation of water-containing isopropanol-n-butanol-ethanol and gasoline blend as a fuel candidate in spark-ignition engine. Appl. Energy **219**, 42–52 (2018)
23. Calam, A., İcingür, Y., Solmaz, H., Yamk, H.: A comparison of engine performance and the emission of fusel oil and gasoline mixtures at different ignition timings. Int. J. Green Energy **12**, 767–772 (2015)
24. Öztöp, H.F., Varol, Y., Altun, Ş., Firat, M.: Using gasoline-like fuel obtained from waste automobile tires in a spark-ignited engine. Energy Sources, Part A Recover. Util. Environ. Eff. **36**, 1468–1475 (2014)
25. Kareddula, K., Puli, R.: Influence of plastic oil with ethanol gasoline blending on multi cylinder spark ignition engine. Alexandria Eng. J. **57**, 2585–2589 (2018)
26. Kareddula, V., Puli, R., Kumari, A., Shailesh, P.: Performance and emission studies of a SI engine using distilled plastic pyrolysis oil-petrol blends. MATEC Web Conf. **45**, 03002 (2016)
27. Suiyuay, C., et al.: Effect of gasoline-like fuel obtained from hard-resin of Yang (*Dipterocarpus alatus*) on single cylinder gasoline engine performance and exhaust emissions. Renew. Energy **153**, 634–645 (2020)
28. Dai, Z., et al.: Introducing a single secondary alcohol dehydrogenase into butanol-tolerant *Clostridium acetobutylicum* Rh8 switches ABE fermentation to high level IBE fermentation. Biotechnol. Biofuels **5**, 1–10 (2012)

29. Butmax. Butamax. <https://www.butamax.com/> (2020)
30. Gevo. Gevo. <https://gevo.com/> (2020)
31. Ye, S., Ma, X., Chen, D., Tao, P.: Influence of rotating speed on pyrolysis products of waste plastics in rotary kiln. *Chinese Soc. Electr. Eng.* (2014). <https://doi.org/10.13334/j.0258-8013.pcsee.2014.23.016>
32. Dobó, Z., et al.: Transportation fuel from plastic wastes: production, purification and SI engine tests. *Energy* **189**, 116353 (2019)
33. Canakci, M., Ozsezen, A.N., Alptekin, E., Eyidogan, M.: Impact of alcohol-gasoline fuel blends on the exhaust emission of an SI engine. *Renew. Energy* **52**, 111–117 (2013)
34. Sivasubramanian, H., Pochareddy, Y.K., Dhamodaran, G., Esakkimuthu, G.S.: Performance, emission and combustion characteristics of a branched higher mass, C3 alcohol blends fuelled medium duty MPFI SI engine. *Eng. Sci. Technol. an Int. J.* **20**, 528–535 (2017)
35. Mourad, M., Mahmoud, K.R.M.: Performance investigation of passenger vehicle fueled by propanol/gasoline blend according to a city driving cycle. *Energy* **149**, 741–749 (2018)
36. Elfasakhany, A.: Performance and emissions analysis on using acetone–gasoline fuel blends in spark-ignition engine. *Eng. Sci. Technol. an Int. J.* **19**, 1224–1232 (2016)
37. Li, Y., Ning, Z., Lee, C., Fon, F., Yan, J., Lee, T.H.: Effect of acetone-butanol-ethanol (ABE)-gasoline blends on regulated and unregulated emissions in spark-ignition engine. *Energy* **168**, 1157–1167 (2019)
38. Yusri, I.M., et al.: Experimental investigation of combustion, emissions and thermal balance of secondary butyl alcohol-gasoline blends in a spark ignition engine. *Energy Convers. Manag.* **123**, 1–14 (2016)
39. Dhamodaran, G., Esakkimuthu, G.S., Pochareddy, Y.K., Sivasubramanian, H.: Investigation of n-butanol as fuel in a four-cylinder MPFI SI engine. *Energy* **125**, 726–735 (2017)
40. Galloni, E., Fontana, G., Staccone, S., Scala, F.: Performance analyses of a spark-ignition engine firing with gasoline-butanol blends at partial load operation. *Energy Convers. Manag.* **110**, 319–326 (2016)
41. Galloni, E., Fontana, G., Scala, F.: Experimental and numerical analyses of a spark-ignition engine firing with N-Butanol-Gasoline Blends at high load operation. *Energy Procedia* **148**, 336–343 (2018)
42. İçingür, Y., Calam, A.: The effects of the blends of fusel oil and gasoline on performance and emissions in a spark ignition engine. *J. Fac. Eng. Archit. Gazi Univ.* **27**, 143–149 (2012)
43. Gong, J., Zhang, Y., Tang, C., Huang, Z.: Emission characteristics of iso-propanol/gasoline blends in a spark-ignition engine combined with exhaust gas re-circulation. *Therm. Sci.* **18**, 269–277 (2014)
44. Elfasakhany, A.: Experimental investigation on SI engine using gasoline and a hybrid iso-butanol/gasoline fuel. *Energy Convers. Manag.* **95**, 398–405 (2015)
45. Abdalla, A.N., Ali, O.M., Awad, O.I., Tao, H.: Wavelet analysis of an SI engine cycle-to-cycle variations fuelled with the blending of gasoline -fusel oil at a various water content. *Energy Convers. Manag.* **183**, 746–752 (2019)
46. Karaosmanoğlu, F., İşiğigür, A., Aksoy, H.: Methanol-unleaded gasoline blends containing fusel oil fraction as spark ignition engine fuel. *Energy Sources* **19**, 567–577 (1997)
47. Turner, J., Pearson, R., McGregor, M., Ramsay, J.: GEM Ternary Blends: Testing Iso-stoichiometric mixtures of gasoline, ethanol and methanol in a production FFV fitted with a physical alcohol sensor. *SAE Technical Papers* <https://www.sae.org/publications/technical-papers/content/2012-01-1279/>(2012). <https://doi.org/10.4271/2012-01-1279>
48. Awad, O.I., et al.: Alcohol and ether as alternative fuels in spark ignition engine: a review. *Renew. Sustain. Energy Rev.* **82**, 2586–2605 (2018)



Operationalizing the Water, Energy and Food Nexus Through the Law

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Abstract. The prevailing system of governance of the water, energy and food sectors is characterized by siloed law, policy and institutional structures, frustrating the transition to a more sustainable approach to resource governance. The past decade saw the emergence of the Water, Energy and Food Nexus (‘WEF Nexus’), an approach promoting the coordinated management and governance across sectors and scales, thereby responding directly to the complex and inseparable interactions and interdependencies between water, energy and food systems. Achieving coordinated governance of WEF resources is a challenging undertaking, one that cannot be effectively operationalized if it not endorsed and implemented through law and policy. Yet, as this paper shows, the law and the legal discipline have, until now, been largely absent from consideration within the WEF Nexus literature. Without understanding what characteristics require reflection within the legal and policy framework to support its operationalization, the WEF Nexus shall remain but a theoretical ideal.

Through a structured literature review of 39 records, this paper identifies the necessary characteristics of a regulatory framework that supports the operationalization of the WEF Nexus. An approach to mapping existing water, energy and food regulatory systems is then designed such that the researcher may determine the extent to which an existing regulatory system reflects the nexus characteristics.

This paper thus argues that the WEF Nexus cannot mature as a concept without taking bold steps towards reaching an understanding of how the Nexus can be applied in practice, which in turn requires the consideration of existing regulatory frameworks. By identifying common characteristics of a nexused governance framework as discerned from existing literature, this research takes a first step towards developing a shared understanding of how the WEF Nexus can be operationalized through the law.

Keywords: WEF Nexus · Law · Coordinated governance · Resource management

1 Introduction

The Water, Energy and Food Nexus (‘WEF Nexus’), though having previously gained some degree of scholarly interest [6, 12, 18], burst onto the academic stage in earnest

in 2011 following *The Water Energy and Food Security Nexus—Solutions for the Green Economy* conference held in Bonn [4, 15]. The widely cited background paper to the conference introduced the WEF Nexus as an approach that ‘integrates management and governance across [WEF] sectors and scales’, thereby moving away from the conventional siloed approach [7]. The potential of the WEF Nexus therefore lies in its promotion of coordinated governance frameworks, which respond directly to the complex and inseparable interactions and interdependencies between water, energy and food. To understand the potential value of the Nexus, these interdependencies are broadly outlined here.

In the most simplistic sense: the generation of electricity and the production of food both utilize large quantities of water, with agriculture utilizing 70% of the world's fresh water supply [5]. Energy is, in turn, required to transport and treat drinking water and to filter wastewater for reuse or safe release into the environment [5]. Simultaneously, climate change places additional stress on food and water supply, which is further exacerbated by the excessive use of carbon fuels in energy production [5]. As such, the actions of, and the constraints imposed within, one sector (energy, water or food) directly impact the other sector(s) owing to cross-sectoral interdependence.

This interdependence is equally reflected at policy level: the policy objectives in one sector are either the preconditions for the realization of another sector's objectives or, alternatively, the policies of one sector constrain or impose conditions on what may be achieved in another sector [15, 19]. In WEF Nexus terms this amounts to a manifestation of cross-sectoral interdependence within the policy realm.

As such, when viewed as an analytical framework, academics involved in the development of the WEF Nexus view it as a lens through which we may identify and understand synergies and trade-offs within both physical WEF systems and WEF related policy. The WEF Nexus thereby aids in improving the governance of WEF resources towards achieving more resilient systems. The WEF Nexus has, however, been criticized for being nothing more than a buzzword, absent of practical applicability [3]. However, in moving from theoretical ideal to implementable framework, law and policy must be considered within nexus discourse. This is because the provision of water, energy and food constitutes a policy realm that is firmly entrenched within existing governing legal texts of statutes and sectoral regulations. Furthermore, the management of water, energy and food systems – particularly when striving for greater coordination in the face of perceived siloism – is nuanced and complex, largely because it involves multiple actors spanning different governance scales.

As such, informal social norms, though powerful, cannot sufficiently ensure appropriate degrees of coordination as is required by the WEF Nexus approach, nor can social norms adequately confront the challenges associated therewith. Though to a lesser extent, official policy proclamations can also not perform the task of hard law. After proceeding on a similar line of analysis, albeit in a different but related theoretical context, Ruhl argues that-

no new theory of how to do things in environmental and natural resources management, particularly one that challenges entrenched ways of doing things and the interests aligned around them, is likely to gain traction in practice if it cannot gain

traction in the form of endorsement and implementation through specific laws and regulations [14].

Similarly, as illustrated by Allan et al., implementing new approaches aimed at ensuring sustainability and/or resilience of resource systems is only effective where supported by adequate regulatory regimes [1]. Thus, without adequate procedural, rights-based or other legal mechanisms for enforcing implementation, the operationalization of the particular framework or approach will stall. Without taking legal considerations into account, there is little hope for the WEF Nexus approach to effectively move from the realm of academic theory to that of practice.

Of further importance in this regard is the need to tailor the translation from theory to law to the political, social and legal culture of the jurisdiction within which the WEF Nexus is being operationalized. Without a thorough understanding of the content, scope and operation of the applicable statutes and regulations within a particular jurisdiction, the existing regulatory barriers to WEF Nexus implementation cannot be foreseen and resolved. This understanding is best achieved by mapping the legal regime regulating WEF resources of a particular jurisdiction to identify the existing barriers and untapped capacities that have the potential to hinder or promote WEF Nexus operationalization.

However, prior to mapping a legal regime, it is necessary to understand what characteristics the WEF Nexus requires reflected therein to promote coordination across sectors. To this end, a structured literature review is conducted to extract the necessary characteristics of a “nexused” regulatory framework that supports coordination across WEF sectors. An approach to mapping existing water, energy and food regulatory systems is then proposed such that the later research may apply this methodology to determine the potential in law to reflect a coordinated approach to WEF resource management.

2 Methodology

As a starting point, this review draws on previous work that I completed alongside Buijze and Malan [2] in which a systematic literature review was conducted based on the PRISMA Statement methodology developed by Moher and others [13]. The primary aim of PRISMA is to ensure that the systematic literature review is conducted objectively, with each decision taken by researchers made explicit, such that the review can be replicated and thus may be checked for validity and reliability.

The aim of the review was to collect and review the top 20% of literature (determined by citation number) published in the English language within peer reviewed journals on the Google Scholar database from 2011 (being the year of the seminal “*The Water Energy and Food Security Nexus—Solutions for the Green Economy*” conference) up to and including June 2021 (being the month immediately prior to the literature being collected) [2]. The Google Scholar database was searched using the key words “water”, “energy”, “food” and “nexus” in all possible combinations, resulting in 3634 records being collected. Duplicates were then removed and screening and eligibility criteria were applied.

Screening criteria required that the record be in the English language, and published in a peer reviewed journal from 2011 up to and including 2021. Eligibility criteria

required that all three spheres of the nexus be addressed in the record, thus those records focusing for example only on a “water energy nexus” or on a “water, energy, food and coal nexus” were excluded. Following screening, 208 records were included in the review. These 208 records thus represent the top 20% of WEF Nexus studies published between 2011 and 2021 judged according to citation number (Fig. 1).

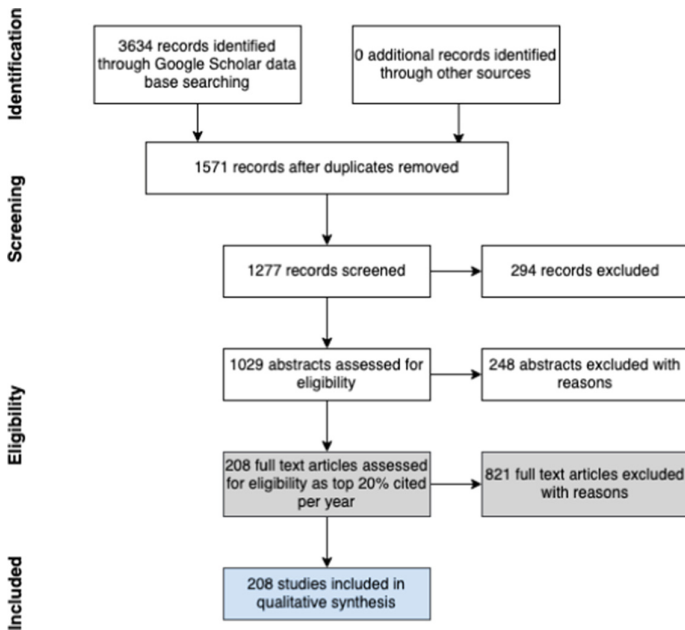


Fig. 1. Results of record collection and screening process according to PRISMA methodology

For the purposes of the present review, I then re-screened each of the 208 abstracts and applied additional eligibility criteria, selecting only those records that, at face value, examined the regulatory, governance, and/or political aspects of the WEF Nexus. This resulted in the selection of 55 records. I then embarked on a detailed and complete reading of each record, resulting in the further exclusion of 16 records for failing to meet the aforementioned eligibility criteria, 39 records thus being included in the final review.

In an EXCEL spreadsheet, the characteristics identified within each record were then recorded alongside the year of publication, updated citation number as of 1 October 2021, the field of study of the research, the definition of the WEF Nexus given, and the methodology adopted in the research. From this data, the ‘common characteristics’ – namely those characteristics identified by two or more records – were identified, the results of which are presented and discussed below.

3 Results

Of the 208 records screened for inclusion in this review, only two were from the field of law with research having been conducted that directly considered the legal aspects

Table 1. Summary of disciplinary field of articles included in review

Total No. of Articles per Field of Study	
Field of Study of Article	Total No. of Articles
Governance	12
Sustainability Studies	2
Environmental Science	12
Interdisciplinary/ Transdisciplinary	4
Law	2
Political Science	5
Critical Social Science*	1
*Article did not contribute characteristics but was kept in review for underlying governance insight.	
Uncategorised	1
Total Articles	39

of the WEF Nexus (*see* Table 1). Those records originating from a disciplinary field other than law either failed to consider or acknowledge legal aspects of the WEF Nexus altogether, or observed a need for legal considerations more generally [11] but did not further the enquiry beyond mere observation. This demonstrates the absence of legal considerations in prevailing WEF Nexus discourse.

This notwithstanding, the literature did sufficiently develop the Nexus from a governance perspective, identifying those characteristics necessary in promoting coordination in WEF systems of governance. Taking an interdisciplinary perspective, the legal field may draw on the characteristics identified as necessary for effective governance and translate this into applicable legal mechanisms. Where a legal mechanism reflects the characteristics that non-legal fields identify as necessary for promoting coordinated resource management, such legal mechanism should serve as an example of a means of promoting coordination through law. In this way the first step towards nexus operationalization is taken, by identifying the kinds of legal mechanisms that promote WEF coordination in the manner envisaged by WEF Nexus proponents.

With this in mind, the characteristics identified in this literature review can be presented. Table 2 gives an overview of the results of the review, including a specification of the number of records per disciplinary field that identified a particular characteristic. A total of twenty characteristics were identified within the literature. Though there was a degree of variance in the terminology used in describing the characteristics – for example “bridging mechanisms” versus “cross-cutting mechanisms” – the variance was small, and the terminology was largely consistent. The most prevalent characteristic identified was the requirement of horizontal/cross-sectoral coordination, which was considered a

necessary element of a nexused regulatory framework in 44% of the records reviewed. The least prevalent characteristics were (predictably) those directly referencing legislation with the requirement for consideration of inter-sectoral issues within legislation, and for localized over generalized legislation and planning identified in only 3 of the 39 records.

The nature of the characteristic(s) identified within a particular record depended largely on the nature and focus of the specific research. This serves as one explanation for why no single characteristic was identified by a majority of records within the review. A second explanation for this is that no record had as its primary aim the identification of the necessary characteristics of a nexused regulatory framework. Instead, such characteristics arose within the discussion of the particular research question explored within

Table 2. Overview of characteristics necessary in promoting a nexused approach to WEF governance

Characteristic Identified in Literature	Field of Study of Article							Total
	Gov	SS	ES	I/T	Law	PS	UC	
horizontal / cross-sectoral coordination	5	2	4	2	1	3		17
incentives for nexused decision making and/or implementation of practices	5	1	5		1	2		14
policy coherence	4	1	4		1	2		12
inter-sectoral cooperation / information sharing	5	1	3		1	1		11
long-term planning (policy approach/objectives) with short term goals and (flexible) planning	3	1	5	2				11
multi-stakeholder engagement (more broadly stated - no specific moment designated)	3	1	3		1	2		10
integrated / inter-sectoral policy / policy making	3	1	3	1		1	1	10
effective institutional structure to facilitate coordination across sectors	3		4		1	1	1	10
public participation / participatory processes or mechanisms	5	1	1			2		9
reliable and consistent data collection in order to clarify interactions and design incentives / nexus approaches	4		3			1	1	9
constant monitoring (either of targets/goals or of impacts)	3		2		1	1		7
sufficient budgetary and financial planning to implement nexus initiatives	3		2	1				6
bridging / cross-cutting mechanisms	2		2	1	1			6
decentralized / localized decision making and nexus implementation	2		1	1	1	1		6
science-based policy making		1	2	1		1		5
flexibility in decision making		2	1	1				4
harmonization of sectoral goals / targets / objectives	3		1					4
clarify rights and responsibilities across sectors	1		1	1	1			4
consideration of inter-sectoral issues within legislation			2		1			3
localized over generalized legislation and planning			1		1	1		3

any given record, and this review extrapolated such characteristics from the general discussion. It is for this reason that a systematic literature review based on the PRISMA methodology was elected such that this review may be reproduced in case it is necessary to test for validity of results.

It should be borne in mind that these results serve as a first step towards formulating the common characteristics of a nexused regulatory framework. It is not the intention or submission of this research that the characteristics identified within this literature review constitute a conclusive, comprehensive and authoritative list. Given that this exercise is a novel one within the WEF Nexus literature, and further that legal and political considerations of the nexus remain in their infancy, it is hoped that this review may serve as inspiration for further research that aims to develop, in more concrete terms, how the Nexus may be applied to regulatory frameworks governing WEF sectors.

4 Discussion

4.1 Analyzing the Characteristics Promoting a WEF Nexus Approach to Resources Management

What becomes immediately clear upon a first reading of the identified characteristics is that they are broadly and normatively stated. This reflects the absence of concrete proposals within the existing literature on how the nexus can be applied to existing governing frameworks. Instead, the literature presents an almost idealized perspective in which the WEF Nexus is utilized as a means of constructing a ‘best case’ alternative to existing siloed governance structures, absent of practical proposals for ‘real-world’ implementation. However, this is not in and of itself problematic.

Instead, theorizing an ideal application of a WEF Nexus approach to WEF resource governance is a necessary initial process of academic and scientific creativity that becomes problematic only when it continues in such a vein *ad infinitum*. This initial process is particularly important where an alternative to the prevailing status quo is being sought, requiring innovative thinking theorizing the ideal governance structure. However, there must reach a point in which this innovatory theory is consolidated and translated into more realistic and practically applicable terms. Given that a decade has passed since the WEF Nexus conference in Bonn and the subsequent sharp uptake in focused research on the topic, the time for more practical translations of the Nexus has come.

This notwithstanding, given that the Nexus requires a jurisdictionally specific and tailored approach, the translation from theory to practice cannot necessarily be a singular endeavor with subsequent universal application. Instead, what is required is the consolidation of the characteristics of a nexused governance framework to serve as a guideline for the class of features required within the regulatory framework in order to operationalize the Nexus. Thereafter, research focused on a specific jurisdiction is necessary to determine more precisely what mechanisms are required in practice taking into account the regulatory and political landscape as well as the prevailing socio-economic realities shaping the extent to which certain mechanisms are realistically implementable.

Therefore, although the normatively framed characteristics require translation to practically implementable mechanisms, such a translation must be tailored to the context

in which the Nexus is being applied. This jurisdictional specificity required may also contribute an explanation as to why characteristics within the literature have, until now, remained broadly and normatively stated.

Beyond the normativity of the characteristics identified, it is also interesting to observe that the listed characteristics do not raise any entirely new ideas within the realm of governance research. In fact, strong similarities can be drawn with the characteristics of adaptive governance [9, 10], risk governance [21], good governance [17], and reflexive governance [20]. However, the existence of parallels does not necessitate the conclusion that the WEF Nexus approach to governance is not sufficiently novel to warrant consideration, nor that it is simply a reproduction of existing approaches wrapped in new terminology. Instead, such similarities represent a wider consensus within the Social Sciences on what is required within a governance framework in order to promote resilient and/or sustainable management of resources.

The Nexus approach, though sharing many characteristics of alternative governance approaches, is distinguishable by its foregrounding of the interlinkages existing between WEF sectors and the need for the regulatory framework to not only account for but also reflect such interlinkages. This results in priority given to *coordination, cooperation and information sharing across WEF sectors* as core characteristics of the requisite governance framework.

Furthermore, the characteristics identified are to a large extent complementary. If read together they promote, as a best-case scenario, *a framework that prioritizes strong horizontal coordination between departments such that sectoral goals and incentives are aligned across departments and decision making is collaborative with open channels for information sharing across sectors and scales*. Importantly, a reading of these characteristics in this way does not necessarily imply a call for greater degree of *integration*. Instead, what is required is mechanisms *promoting inter-sectoral collaboration, coordination and cohesion*, the precise degree of which should be determined by the existing institutional and regulatory landscape of a particular jurisdiction.

By way of example, achieving a high level of coordination may be impractical in a Sub-Saharan African context where institutional capacity is limited, but a more realistic endeavor in a more developed western-European context. Thus, the degree of coordination encouraged by the nexused governance approach should be viewed as a sliding scale, the precise positioning on the scale between higher or lower levels of coordination being dependent on the jurisdictional and institutional realities of the region of application.

This systematic literature review has thus provided a first step towards formulating the common characteristics of a nexused regulatory framework. Additionally, the results and discussion thereof serve as a basis for which this research may move forward in mapping the existing law governing the WEF sectors.

As has been emphasized in the discussion herein, translation from theory to practice requires a jurisdictionally specific and tailored approach. It is for this reason that I have not at this stage proposed definitive mechanisms that may promote a nexused governance framework in a general sense. Instead, using the characteristics identified in this review as a *guideline*, the existing regulatory system of a particular jurisdiction can be analyzed to determine to what extent and in what way these characteristics are already reflected

within the jurisdiction, the converse of which gives insight into the aspects of that existing regulatory framework that may present barriers to achieving nexused governance of WEF sectors.

4.2 A Methodology for Mapping the Potential for Existing Regulatory Frameworks to Promote the WEF Nexus Approach to Resource Governance

Methodological Design. The difficulty in mapping the legal framework shaping the governance of WEF resources is the sheer volume of legal instruments that may fall within the scope of the review. The extent of the review will thus hinge on the capacity of a research project. As a minimum, however, the core or steering legislation within each WEF sector respectively should be analyzed.

As a general guideline, legislation and policy designating technical requirements, for example technical standards for water storage or food safety and labeling requirements, need not be included within the review. Priority should be given to legal instruments regulating the WEF sectors with potential to promote cross-sectoral coordination, namely instruments regulating decision-making within WEF sectors; WEF service delivery and end-use of the resource(s); and infrastructure planning and management of WEF resources. This is not to say that technical standards do not represent an area of law with the potential to promote coordination, but rather that given the breadth of legislation applicable to WEF sectoral regulation, certain scoping decisions may be necessary and technical specifications represents a class of legislation reasonably excludable.

Additionally, an analysis of sectoral legislation should be conducted against the backdrop of applicable overarching legislative frameworks, such as within the branches of administrative and constitutional law, which shape the exercise of public power. Other overarching areas of law that may be applicable include regulatory instruments providing for environmental conservation and/or environmental management, disaster management, and land use planning laws.

Once the legislation of the analyzed jurisdiction is selected, each document should be reviewed, identifying legal mechanisms that either reflect or have the effect of promoting one or more of the characteristics identified herein. In this way, the identified characteristics help to guide the researcher in recognizing untapped potential within the law to promote a nexused approach to WEF governance.

This methodology is applied to map the overarching administrative law applicable to the regulation of public powers in the South African legal context as a mini-case study analysis to illustrate how the identified characteristics may be useful in informing an enquiry into the extent to which existing legal frameworks facilitate the operationalization of the WEF Nexus. Indeed, the wider the legislative review, the more reflective the findings of the potential barriers and untapped capacities within the existing legal system. As such this mini-case study serves only to illustrate the application of this methodology and the of the characteristics identified within the above literature review.

South African Administrative Law as a Case Study. I begin by selecting the applicable regulatory instrument to include within the review. The regulatory instrument's selection is then motivated, followed by a brief summary of the most important provisions

identified within, given that such provisions reflect one or more of the characteristics identified as promoting a WEF Nexus approach to resource governance.

Since South Africa is a constitutional democracy, the most important legislative instrument is the Constitution of South Africa [22] and is thus a clear starting point for the review. The Constitution establishes the overall framework for the exercise of public power, the most important sections in this regard being Sections 33 and 195. Section 33 establishes a right to just administrative action that is 'lawful, reasonable and procedurally fair' (Section 33(1)), and obligates government to enact legislation giving effect to this right (Section 33(3)). Section 195 sets out the basic values and principles governing public administration which includes requirements for the public administration to promote the '[e]fficient, economic and effective use of resources' (Section 195(1)(b)); the impartial, fair, equitable and unbiased provision of services (Section 195(1)(d)); and the participation of the public in policy-making (Section 195(1)(e)). Any legislation enacted that regulates public administration must, per Section 195(3), promote these principles and values.

The law giving effect to the Section 33 right, and that complies with the Section 195 principles and values, is the Promotion of Administrative Justice Act [24] ('PAJA'). Given that the Constitution requires its enactment, PAJA is clearly required within the legislative review.

PAJA is a law of general application. This means that it applies to and binds the entire government administration across all spheres (national, provincial and local), and further that it does not grant powers to administrators but instead provides *how* the powers given to administrators *by other laws* must be exercised. PAJA sets out in detail what steps must be taken by public officials for administrative action to be considered lawful, reasonable and procedurally fair (Sections 3 and 4). The Act further empowers individuals to take a public decision/action on review in court (Sections 6 and 7), and/or to request reasons for the public decision/action (Section 5).

Furthermore, for administrative action affecting the public to meet the threshold of procedural fairness, PAJA requires the public official hold a public enquiry and/or a notice and comment procedure thereby entrenching participatory process into the public decision-making procedure. This applies regardless of whether the applicable sectoral legislation requires participatory process or not. Procedural fairness is thus concerned with participation in decisions that affect an individual's rights and/or legitimate expectations [8].

The final legislative instruments selected for review were the Intergovernmental Relations Framework Act [23] ('IRF Act'), Intergovernmental Fiscal Relations Act [24] ('IFR Act'), and The Local Government: Municipal Systems Act [26] ('MS Act'). This trio of legislation was selected given that it collectively regulates and co-ordinates the relations across the three scales of government and promotes a system of cooperative government. The promotion of co-ordination across scales is directly relevant given that WEF sectors are differently organized across all levels of government. Co-ordination is promoted within this legislation through-

- mandated consultation across spheres and organs of government when conducting affairs and/or drafting and implementing legislation and policy (for example Sections 5(b), 5(e), and 36 of the IRF Act);
- established intergovernmental consultative forums or bodies (for example Sections 6 and 16 of the IRF Act, and Sections 2, 3 and 5 of the IFR Act), and the correlating legal obligation to actively participate in these intergovernmental structures (Section 5(f)(i) IRF Act);
- the legal obligation for co-ordination across government scales and departments when implementing legislation and/or policy (Section 5(c) IRF Act) in order to promote coherence in governance across spheres (Section 4(a) IRF Act);
- the legal obligation to cooperate with information sharing requests across government scales (Sections 5(e)(i) and (ii) IRF Act);
- the empowerment of organs of state to enter into an implementation protocol that defines ‘the roles and responsibilities of each organ of state in implementing policy, exercising the statutory power, performing the statutory function or providing the service’ (Sections 35 IRF Act); and
- the requirement that planning undertaken by a municipality be aligned with and complement ‘the development plans and strategies of other affected municipalities and other organs of state’ (Section 24(1) of the MS Act).

An important finding is thus made: the administrative law shaping the governance of WEF sectors in South Africa reflects a number of the nexus characteristics and the existing legal mechanisms hold potential to promote a coordinated governance approach. However, this coordinated approach is more strongly applied across scales than across sectors. Sectoral legislation thus needs to be examined to determine if sectoral coordination is promoted therein. Importantly, despite an presence of mechanisms actively promoting intersectoral coordination, no significant legal barriers were found in the administrative law framework that prevent this from being pursued. This represents an area of potential for future legal development. A more detailed discussion of this potential, however, must be deferred to a later extensive review, following the completion of the analysis of the sectoral legislation and policy.

5 Conclusion

The above analysis has clearly demonstrated an absence of legal considerations within prevailing WEF Nexus literature. Given that WEF governance is embedded within extensive regulatory frameworks, legal considerations within WEF Nexus discourse are necessary to enable its operationalization as an approach to resource governance. A first step in this regard is to acknowledge what characteristics require reflection within prevailing regulatory frameworks in order to promote a nexused approach to WEF governance. Having identified 20 characteristics within prevailing literature, it is important to map the regulatory regime shaping the governance of WEF resources in a particular jurisdiction to determine the extent to which such characteristics are already reflected. This in turn generates insight into what aspects of the prevailing legal system hold potential to promote a coordinated governance approach, and what aspects may present barriers to

implementing such an approach and thus require targeted legal reform. In this way, this paper has taken a first step towards developing a shared understanding of how the WEF Nexus can be operationalized through the law.

Appendix: Articles included in systematic review (n = 39)

	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> 01/10/2021	Field of study
1	Allouche, J; Middleton, C; Gyawali, D	Technical Veil, Hidden Politics: Interrogating the Power Linkages behind the Nexus	2015	196	Political Science
2	Artioli, F; Acuto, M; Mcarthur, J	The water-energy-food nexus: An integration agenda and implications for urban governance	2017	89	Political Science
3	Bhaduri, A. and Others	Sustainability in the water-energy-food nexus	2015	97	Governance
4	Bréthaut, C.; Gallagher, L.; Dalton, J.; Allouche, J	Power dynamics and integration in the water-energy-food nexus: Learning lessons for transdisciplinary research in Cambodia	2019	26	Interdisciplinary
5	Cairns, R.; Krzywoszyńska, A	Anatomy of a buzzword: the emergence of 'the water-energy-food nexus' in UK natural resource debates	2016	217	Governance
6	Daher, B. and Others	Towards bridging the water gap in Texas: A water-energy-food nexus approach	2019	39	Governance
7	de Andrade, G. and Others	A literature-based study on the water–energy–food nexus for sustainable development	2021	20	Sustainability Studies

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	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> <u>01/10/2021</u>	Field of study
8	Foran, Tira	Node and Regime: Interdisciplinary Analysis of Water-Energy-Food Nexus in the Mekong Region	2015	110	Critical social sciences
9	Howarth, C.; Monasterolo, I	Opportunities for knowledge co-production across the energy-food-water nexus: Making interdisciplinary approaches work for better climate decision making	2017	84	Interdisciplinary
10	Howarth, C.; Monasterolo, I	Understanding barriers to decision making in the UK energy-food-water nexus: The added value of interdisciplinary approaches	2016	141	Governance
11	Kaddoura, S; El Khatib, S	Review of water-energy-food Nexus tools to improve the Nexus modelling approach for integrated policy making	2017	109	Uncategorized
12	Keskinen, M. and Others	The Water-Energy-Food Nexus and the Transboundary Context: Insights from Large Asian Rivers	2016	100	Political Science

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	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> <u>01/10/2021</u>	Field of study
13	Kurian, M	The water-energy-food nexus: trade-offs, thresholds and transdisciplinary approaches to sustainable development	2017	206	Governance
14	Kurian, M. and Others	One swallow does not make a summer: Siloes, trade-offs and synergies in the water-energy-food nexus	2019	26	Environmental Science
15	Larcom, S; van Gevelt, T	Regulating the water-energy-food nexus: Interdependencies, transaction costs and procedural justice	2017	37	Law
16	Leck, H; Conway, D; Bradshaw, M; Rees, J	Tracing the Water-Energy-Food Nexus: Description, Theory and Practice	2015	333	Environmental Science
17	Leese, M; Meisch, S	Securitising Sustainability? Questioning the 'Water, Energy and Food-Security Nexus'	2015	133	Political Science
18	Liu, J. and Others	Nexus approaches to global sustainable development	2018	254	Sustainability Studies
19	Mercure, J.F. and Others	System complexity and policy integration challenges: the Brazilian Energy-Water-Food Nexus	2019	79	Interdisciplinary

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	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> <u>01/10/2021</u>	Field of study
20	Middleton, C; Allouche, J; Gyawali, D; Allen, S	The Rise and Implications of the Water-Energy-Food Nexus in Southeast Asia through an Environmental Justice Lens	2015	101	Environmental Sciences
21	Mohtar, R.H.; Daher, B	Water-Energy-Food Nexus Framework for facilitating multi-stakeholder dialogue	2016	84	Transdisciplinary
22	Newell, Joshua P.; Goldstein, B.; Foster, A	A 40-year review of food-energy-water nexus literature and its application to the urban scale	2019	57	Governance
23	Nhamo, L. and Others	The Water-Energy-Food Nexus: Climate Risks and Opportunities in Southern Africa	2018	89	Environmental Science
24	Olawuyi, D	Sustainable development and the water-energy-food nexus: Legal challenges and emerging solutions	2020	20	Law
25	Pahl-Wostl, C	Governance of the water-energy-food security nexus: A multi-level coordination challenge	2019	179	Environmental Science
26	Pardoe, J. and Others	Climate Policy Climate change and the water-energy-food nexus: insights from policy and practice in Tanzania	2018	71	Governance

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	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> <u>01/10/2021</u>	Field of study
27	Rasul, G	Managing the food, water, and energy nexus for achieving the Sustainable Development Goals in South Asia	2016	298	Environmental Science
28	Rasul, G.; Sharma, B	The nexus approach to water-energy-food security: an option for adaptation to climate change	2016	387	Governance
29	Salmoral, G. and Others	Water diplomacy and nexus governance in a transboundary context: In the search for complementarities	2019	19	Governance
30	Scott, C.A.; Kurian, M.; Wescoat, J.L	The Water-Energy-Food Nexus: Enhancing Adaptive Capacity to Complex Global Challenges	2015	180	Governance
31	Sharmina, M. and Others	A nexus perspective on competing land demands: Wider lessons from a UK policy case study	2016	57	Environmental Science
32	Smidt, S. J. and Others	Complex water management in modern agriculture: Trends in the water-energy-food nexus over the High Plains Aquifer	2016	89	Environmental Science
33	van Gevelt, T	The water-energy-food nexus: bridging the science-policy divide	2020	24	Political Science

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	<u>AUTHOR(S)</u>	<u>TITLE</u>	<u>YEAR</u>	<u>CITATION</u> <u>01/10/2021</u>	Field of study
34	Venghaus, S; Hake, J.F	Nexus thinking in current EU policies – The interdependencies among food, energy and water resources	2018	56	Environmental Science
35	Weitz, N.; Strambo, C.; Kemp-Benedict, E; Nilsson, M	Closing the governance gaps in the water-energy-food nexus: Insights from integrative governance	2017	210	Governance
36	White, D.D. and Others	Stakeholder Analysis for the Food-Energy-Water Nexus in Phoenix, Arizona: Implications for Nexus Governance	2017	53	Governance
37	Wichelns, D	The water-energy-food nexus: Is the increasing attention warranted, from either a research or policy perspective?	2017	197	Environmental Science
38	Yung, L. and Others	How methods for navigating uncertainty connect science and policy at the water-energy-food nexus	2019	23	Environmental Science
39	Zhang, P. and Others	Food-energy-water (FEW) nexus for urban sustainability: A comprehensive review	2019	115	Environmental Science

References

1. Allan, T., Keulertz, M., Woertz, E.: The water–food–energy nexus: an introduction to nexus concepts and some conceptual and operational problems. *Int. J. Water Resour. Dev.* **31**, 301–311 (2015)
2. Buijze, A., Harvey, N., Malan, G.: Citation pending (2022)
3. Cairns, R., Krzywoszynska, A.: Anatomy of a buzzword: the emergence of “the water-energy-food nexus” in UK natural resource debates. *Environ. Sci. Policy* **64**, 164–170 (2016)
4. Endo, A., et al.: A review of the current state of research on the water, energy, and food nexus. *J. Hydrol. Reg. Stud.* **11**, 20–30 (2017)
5. Finley, J.W., Seiber, J.N.: The nexus of food, energy, and water. *J. Agric. Food Chem.* **62**, 6255–6262 (2014)
6. Hellegers, P., et al.: Interactions between water, energy, food and environment: evolving perspectives and policy issues. *Water Policy* **10**, 1–10 (2008)
7. Hoff, H.: Understanding the nexus. In: Bonn 2011 Conference: The Water, Energy and Food Security Nexus Solutions for the Green Economy. Stockholm Environment Institute. (2011)
8. Hoexter, C., Penfold, G.: *Administrative Law in South Africa*. Juta and Company, South Africa (2021)
9. Hurlbert, M.A.: Adaptive governance (management, co-management and anticipatory). In: *Adaptive Governance of Disaster*. WGCMP, pp. 21–48. Springer, Cham (2018). https://doi.org/10.1007/978-3-319-57801-9_2
10. Janssen, M., van der Voort, H.: Adaptive governance: towards a stable, accountable and responsive government. *Gov. Inf. Q.* **33**(1), 1–5 (2016)
11. Leck, H., et al.: Tracing the water–energy–food nexus: description. *Theor. Pract. Geogr. Compass* **9**, 445–460 (2015)
12. Lopez-Gunn, E., De Stefano, L., Llamas, M.R.: The role of ethics in water and food security: balancing utilitarian and intangible values. *Water Policy* **14**, 89–105 (2012)
13. Moher, D., et al.: Preferred Reporting Items for Systematic Reviews and Meta-Analyses: The PRISMA Statement. *PLOS Med.* **6**, e1000097 (2009)
14. Ruhl, J.B.: Panarchy and the Law. *Ecol. Soc.* **17**, 6 (2012)
15. Scott, A.: Making governance work for water–energy–food nexus approaches. *Climate and Development Knowledge Network: Working Paper* (2017)
16. Scott, Christopher A., Kurian, Mathew, Wescoat, James L.: The water-energy-food nexus: enhancing adaptive capacity to complex global challenges. In: Kurian, Mathew, Ardakanian, Reza (eds.) *Governing the Nexus*, pp. 15–38. Springer, Cham (2015). https://doi.org/10.1007/978-3-319-05747-7_2
17. Shields, B.P., Moore, S.A., Eagles, P.F.J.: Indicators for assessing good governance of protected areas: insights from park managers in western Australia. *Parks* **22**, 37–50 (2016)
18. Siegfried, T.U., et al.: An entitlement approach to address the water-energy-food nexus in rural India. In: *AGU Fall Meeting Abstracts H11G* (2008)
19. Villamayor-Tomas, S., et al.: The water-energy-food security nexus through the lenses of the value chain and the institutional analysis and development frameworks. *Water Altern.* **8**(1), 135–155 (2015)
20. Voß, J., Bauknecht, D., Kemp, R.: *Reflexive Governance for Sustainable Development*. Edward Elgar Publishing, Cheltenham (2006)
21. Walker, G., Tweed, F., Whittle, R.: A framework for profiling the characteristics of risk governance in natural hazard contexts. *Nat. Hazards Earth Syst. Sci.* **14**, 155–164 (2014)

Legislation

22. Constitution of the Republic of South Africa
23. Intergovernmental Relations Framework Act 13 of 2005
24. Intergovernmental Fiscal Relations Act 97 of 1997
25. Promotion of Administrative Justice Act 3 of 2000
26. The Local Government: Municipal Systems Act 32 of 2000



Digital Fabrication in Construction Industry in Africa

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Abstract. Over the past few years, construction has been undergoing a digital revolution by integrating innovative technologies and new construction processes, such as Additive Manufacturing (AM), also called 3D Printing (3DP). The need to advance the green transition towards a more circular economy has been pressing the construction sector to adopt low embodied carbon materials and reduce waste and environmental impact. Earth-based materials have been used for centuries in sustainable constructions in Africa. On the other hand, digitalization is emerging with the support of FabLabs and Fabbers' Schools. These focus on environmentally awareness training programs and developing interconnectedness among sustainable constructions and digital construction technologies. A brief review of the current developments of digital fabrication in Africa is carried out to identify current advancements in digital construction, particularly regarding 3D Printing. AM implementation in the construction sector can improve productivity, automation, and safety, reducing construction times and waste. 3DP can be an enabler for economic progress towards a more sustainable industrialization.

Keywords: Digital fabrication · 3D printing in Africa · Low embodied carbon materials

1 Introduction

Over the past decades, construction practice has been mainly based on manual labour, which is one of the reasons why construction activity is seen as low-tech with small levels of innovation and modernization. Furthermore, it is characterized by many interrelated construction processes, multiple stakeholders, and single barriers, affecting the overall productivity at different construction stages, which makes it a very complex one (Aryicci and Coates 2012; Dallasega et al. 2018; Davila Delgado et al. 2019). As a result, the construction industry faces considerable challenges in improving overall productivity and efficiency. Therefore, it is critical to adopt digital tools, such as AM, Building Information Modelling (BIM), and Virtual Reality (VR), which are already being implemented

on a large scale by other industries like the manufacturing, aerospace, and automotive sector (Barbosa et al. 2017; Dallasega et al. 2020).

Barbosa et al. (2017) and Maskuriy et al. (2019) stress that 3DP in construction can increase productivity and enhance innovation. Many other works highlight the advantages of implementing 3DP in construction to achieve building optimization and essential environmental benefits on 3D printed components and structural elements (Gomaa et al. 2021; Wu et al. 2016). Using earthen building materials and AM it will provide a more sustainable production to replace the current, more popular cement-based products (Veliz Reyes et al. 2019). 3DP of earthen materials includes various sustainable raw materials, such as sand, clay, rammed earth, adobe, and cob. Adding organic fibres to the earthen materials will enhance their mechanical properties, improving thermal and structural performance (Gomaa et al. 2021). The use of 3DP with natural materials has shown promising results suggesting a good performance (Faksawat et al. 2021; Manikandan et al. 2020), though still in its infancy.

Digital Fabrication is broadly used in industrial manufacturing, holding great potential for future construction automation. In addition, digital fabrication can allow the implementation of additional functions on the building structures, such as thermal or acoustic performance, adding value and freedom to architecture (Agustí-Juan and Habert 2017). Digital fabrication has several advantages and limitations for the construction industry, as illustrated in Table 1.

Table 1. Advantages and limitations of 3DP in construction.

Advantages	Limitations	References
Less building times are required to build structural walls	Structure deformation due to poor adhesion, hardening process, and self-weight	(Buswell et al. 2007; Suiker 2022; Suiker et al. 2020)
Fewer pollutant emissions during production	Void creation during extrusion and density reduction of 3DP materials	(Bos et al. 2016; Chaunier et al. 2018; Colorado et al. 2020; Han et al. 2021)
Reduction of material usage and waste	Limited types of materials can be used	(Bedarf et al. 2021; Craveiro et al. 2019; Wang et al. 2016)
Freedom in complex shape designs at convenient costs	Not much research to assure the affordability of 3DP mass implementation	(Keating 2018; Wu et al. 2016)
Optimization of thermal and acoustic properties of buildings	Insulation installation for nonlinear structures	(Craveiro et al. 2017; Kaszynka et al. 2019; Yang et al. 2019)
Promoting work safety and health	3DP building codes and standards	(Guimaraes et al. 2021; Kidwell 2017)
Increase the possibility of recycling compared to conventional buildings		(Muhammad Salman et al. 2021; Yao et al. 2020)

This work aims to give a brief overview of the current state-of-the-art digital fabrication in Africa, particularly regarding the use of 3DP in the construction sector. In addition, it also aims to acknowledge how creative ideas and projects are boosting innovation and encouraging the next generation of Africa's manufacturing skilled workers through collaborations Industry-University.

2 Current State of Digital Fabrication in Africa

Industry 4.0 is a broad concept embracing two main pillars, design principles and technology (Culot et al. 2020). Industry 4.0 portrays an ongoing Industrial Revolution with the digital transformation of industrial processes, such as AM (Ching et al. 2022). According to Deloitte, industry 4.0 will substantially impact Africa's coming years, though the current adoption of digital technologies in construction is still low. Nevertheless, the South African construction industry is one of the most advanced in Africa. Table 2 illustrates the current usage of smart technologies, namely in advanced robotics and 3DP (McKinsey 2020).

Table 2. Current stage of advanced robotics and 3DP in South Africa (McKinsey 2020).

Current usage of smart technologies in the South African construction industry	
Advanced robotics	<ul style="list-style-type: none"> • Low implementation of advanced robotics across different manufacturing sectors • Adoption of robotics is not yet at an advanced stage • Only a few industries like automotive adopt advanced automation/robotics technology • Cost factors are an unaffordable adoption issue for many South African manufacturers
3D printing	<ul style="list-style-type: none"> • No extensive implementation of 3D Printing yet in the construction industry • Actual usage is exclusively used in rapid prototyping, testing of design options, or understanding engineering problems better • Affordability remains the central issue in developing markets • More investments by manufacturers are expected once the cost of 3D Printing machinery comes down

South Africa's progress regarding 3DP in construction has benefited from the governmental support from the Rapid Product Development Association of South Africa (RAPDASA), which commissioned a roadmap in 2013 entitled "South African Additive Manufacturing Technology Roadmap" (Raji 2017). As a result, 3DP was used to enhance productivity and efficiency and produce parts for conventional manufacturing. Currently, South Africa is considered globally competitive in polymer-based and metal-based Additive Manufacturing.

In Kenya, universities play a key role in the current development of digital fabrication, namely 3DP. The African Centre of Technology Studies (ACTS), has collaborated with

Kenyatta University (KU) to establish a 3DP technology centre aiming to advance 3D Printing for industrial capacity building and IT development (Kolade et al. 2022). This network can boost Africa's economic growth and 3DP adoption (Demissie 2017).

In Malawi, the UK-based CDC Group and LafargeHolcim created a joint venture named 14Trees to improve sustainable building solutions. This project introduces 3DP technology to produce sustainable building infrastructures through 3DP extrusion (Thawer 2021). This project has already produced a 3D printed house and a school and plans to expand to other African countries, including Kenya and Zimbabwe. The 3D printed school in Malawi took 18 h to build and has been functional since June 2021.

In 2019, the city of Benguerir in Morocco hosted the first edition of the "Solar Decathlon Africa" to promote renewable energy in the construction industry. In this event, the "Be More 3D" start-up company built a 3D printed house with 32 m² in less than 12 h. This achievement allows it to get a prize for the most innovative start-up, awarded by Green Africa Innovation Booster of IRESEN, the Morocco Research Institute (Mélanie 2019).

2.1 Earthen Materials in Morocco, Tunisia, and Algeria

Over centuries, raw earth construction materials have been used in houses, mainly due to their minimal carbon footprint, low thermal conductivity, and good hygroscopic properties. Raw earth materials are among the oldest building materials used for centuries worldwide. Different building techniques are being optimized, ranging from adobe or rammed earth buildings to cob houses and compressed earth block homes. Earthen construction holds great importance to southern Morocco's heritage and architectural traditions, a unique image of the country's landscape and culture. In recent years, there has been increasing use of earthen materials in construction due to their distinctive properties, availability, and environmentally friendly properties (Parlato et al. 2021), with considerable sustained durability (Zhang et al. 2019).

An excellent example of earthen architecture in southern Morocco is the Ksar of Ait-Ben-Haddou. In the Ouarzazate province, an assembly of earth-based buildings surrounded by high walls representing a traditional way of building technique (UNESCO 2021), preserving its architectural legitimacy. In Morocco, traditional architecture is encouraged as it is resilient to climate change in harmony with the natural and social environment.

Some research works have been investigating the effects of mixing earthen materials with different types of fibres, such as sisal fibres, date palm fibers, olive waste, straw fibers, alfa fibres, plant fibres, and cellulose pulp fibres (Ajouguim et al. 2021; Ben Zaid et al. 2020). Findings prove that implementing these fibres increases both compressive and tensile strength, physical and mechanical characteristics, enhancing thermal performance. (Koutous and Hilali 2021; Lamrani et al. 2019; Millogo et al. 2014; Ouakarrouch et al. 2020; Ramakrishnan et al. 2021; Stanislas et al. 2021).

According to Abid et al. (2021), earth-based construction materials are encouraged in Tunisia due to their unique properties. Providing a new raw material with less carbon footprint, such as compressed earth brick (CEB), exhibiting a compressive strength higher than 2.3 MPa at 28-day tests (Abid et al. 2021).

In Algeria, these traditional building techniques are used, including clay, one of the most well-known building materials in the country, due to its good thermal properties and broad availability (Mansouri et al. 2017). However, a recent study by (Hadji et al. 2020) investigated the thermal conductivity of Algerian desert soil with different amounts of straw in the region of M'Sila. It was observed that mixing straw in the earthen material reduces its thermal conductivity, thus supporting earthen materials over conventional building techniques.

2.2 African Digital Fabrication Laboratories

Most African countries lack essential technological and industrial skills, so there is a need to develop innovative technologies, such as 3D Printing and automation, to reach higher levels of industrialization. African economies have few supply points connected to global supply chains, so they must embrace a radical industrial transformation. Developing the relevant worker skills, infrastructure, and corporate capabilities is gradual and promising. Africa must pursue distinct strategies to achieve industrial relevance towards the industrial revolution (Gadzala 2018).

Several African FabLabs incorporate the digital revolution, drive innovation, provide updated manufacturing knowledge, prototype machinery and software, and train local experts to support novel ideas and projects. In addition, workshops were carried out to support and motivate African youth, students, children, and teenagers.

According to Leyronas (2018), Sésamé Koffi Agodjinou, founder of a start-up “Woe-Lab” in Togo, FabLabs is a way to rethink cities designed and shaped by rural regulations. Guiako Obin, the creator of the start-up “BabyLab” in the Ivory Coast, selected the deprived city of Abidjan to create a Fablab and highlight it as a driver for social transformation towards better education and development. The so-called “Blolab” in Bénin, created by Médard Agbayazon, aims to stimulate digital literacy amongst young people and local experts to find better solutions for rural buildings.

A study was conducted on 23 African FabLabs to evaluate strengths and weaknesses, and its strengths are illustrated in Fig. 1. It can be observed that “Team quality and skills” are the major strength with 20%. These FabLabs are located over many regional regions of Africa, namely Morocco, Senegal, Mauritania, Kenya, Benin, Ethiopia, Namibia, Tunisia, Togo, Burkina Faso, Rwanda, Egypt, Niger, and Nigeria.

According to Oladele-Emmanuel et al. (2018), this movement is a key opportunity for Africa's development and industrialization, with beneficial effects on the economy, education, and citizen involvement, namely through training and entrepreneurship (Oladele-Emmanuel et al. 2018). One of the strengths of FabLab in Africa is being led by qualified people with highly technical and human skills, where manufacturing and learning needs are one of the most promising opportunities. However, there are significant threats such as financial resources, clear business models, and political issues.

Ben Rejeb and Roussel (2018) conducted a case study that surveyed North African engineering universities using creativity workshops and FabLabs. This study investigated the impacts of European cooperation programs by setting up education and training programs on seven North African universities in different countries, like Morocco, Tunisia, and Algeria, in collaboration with eight European Universities. The program,

entitled Tempus i-Cré@ project, achieved its primary goals by providing training to university teachers universities, developing new courses, introducing innovation platforms, supporting education and research on design and innovation management. The implementation of FabLabs in the Maghreb universities was a big success, providing material support for designers and innovators (Ben Rejeb and Roussel 2018).

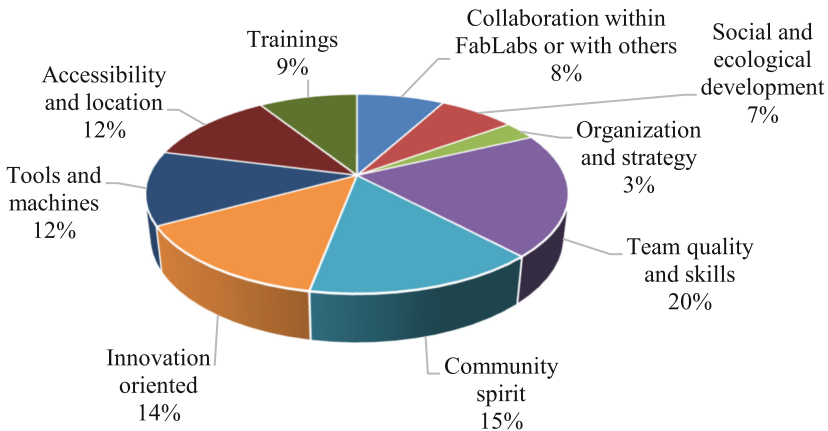


Fig. 1. FabLabs' strengths patterns, adapted from Oladele-Emmanuel et al. (2018).

2.3 African Fabbers School

African Fabbers Schools (AFS) are the first schools in Africa on urban ecologies, self-construction, and digital fabrication. AFS initially started as an itinerant initiative, travelling through different African countries, such as Senegal, Morocco, Mali, Burkina Faso, and many others.

This school project, directed by Paolo Cascone, was developed with an urban fabrication laboratory. According to architect Cascone, the project was conducted under the framework of CAMon program, an initiative promoted by the Centro Orientamento Educativo (NGO CEO). This project aimed to respond to the lack of design schools in the region, focusing on an ecological program and exploring the interaction between material systems in Africa and digital manufacturing technologies (Cascone 2022). In a circular economy context, this kind of school is an opportunity for African economies to develop "local industries" to generate new labour opportunities for the locals. It also explores new home-based designs as a paradigm for digital fabrication and sustainable construction, which could be exported for European markets (Future Architecture Platform 2022). Figure 2 shows a lightweight structure considered a tensile fabric shelter, designed for Salé public garden. Based on the traditional cable system to generate shade solutions in the ancient medina, this project was intended to create an interactive space with the local community.

On the other hand, the project called "The Earth Playground" was initiated at the Sourgoubila Primary School in Burkina Faso, where Cascone has teamed up with experts



Fig. 2. Khaima Urban Tent in Salé (Morocco) (Cascone 2022).

to develop a design for a playground incorporating different aspects of local fabrication as well computational processes. According to Cascone, most of the wood used to make Italian furniture comes from Cameroon. The aim was to transform the wood locally into sustainable house furniture, so a digital fabrication laboratory was implemented in the country, allowing print materials to be printed using additive and subtractive technologies. Supporting this project idea, Prof. Neil Gershenfeld from MIT, USA, believed that the digital revolution was not additive versus subtractive manufacturing technologies. Instead, it evolved from the ability to turn data into things and things into data (Design Indaba 2022; Gershenfeld 2012).

3 Conclusions

A brief review was conducted to understand better the progress of Digital Fabrication in the construction industry in Africa. Digital Fabrication has undergone a substantial evolution in recent years. The number of projects completed and ongoing show that this technology will be of significant importance for the construction sector in the next few years. The integrated digital design and fabrication process (i.e., a design-to-production) can provide more controllability and flexibility during construction. It can bring an innovative perspective to the construction industry in Africa, bringing several advantages on health, cost, climate change, reducing construction times and waste.

Creative ideas and projects are encouraging the next generation of Africa's manufacturing skilled workers through collaborations Industry-University, such as the Digital FabLabs and African Fabbers Schools, fostering innovation and offering good opportunities for economic growth and sustainable development, driving the industry into the future industrialization of Additive Manufacturing in the continent. The African region can emerge as the following factory of the world through Industry 4 technologies, increasing overall productivity and potentially leading to a repositioning of global supply chains.

References

- Abid, R., Kamoun, N., Jamoussi, F., El Feki, H.: Fabrication and properties of compressed earth brick from local Tunisian raw materials. *Boletín de La Sociedad Española de Cerámica y Vidrio* (2021)
- Agustí-Juan, I., Habert, G.: Environmental design guidelines for digital fabrication. *J. Clean. Prod.* **142**, 2780–2791 (2017)
- Ahmed, Z.Y., Bos, F.P., Wolfs, R.J.M., Salet, T.A.M.: Design considerations due to scale effects in 3D concrete printing. In: 8th ASCAAD Conference Proceedings, pp. 115–124 (2016)
- Ajouguim, S., et al.: Effect of Alfa fibers on the mechanical and thermal properties of compacted earth bricks. *Mater. Today: Proc.* **37**, 4049–4057 (2021)
- Arayici, Y., Coates, P.: Virtual Reality: Human Computer Interaction (Tang, X.-X. ed.). InTech (2012)
- Barbosa, F., Woetzel, J., Mischke, J.: Reinventing construction: a route of higher productivity (2017)
- Ben Rejeb, H., Roussel, B.: Design and innovation learning: case study in North African engineering universities using creativity workshops and fabrication laboratories. *Procedia CIRP* **70**, 331–337 (2018)
- Ben Zaid, Z., Tilioua, A., Lamaamar, I., Ansari, O., Souli, H., Hamdi Alaoui, M.A.: An experimental study of the efficacy of integrating a phase change material into a clay-straw wall in the Drâa-Tafilalet Region (Errachidia Province), Morocco. *J. Build. Eng.* **32**, 101670 (2020)
- Bos, F., Wolfs, R., Ahmed, Z., Salet, T.: Additive manufacturing of concrete in construction: potentials and challenges of 3D concrete printing. *Virtual Phys. Prototyping* **11**, 209–225 (2016)
- Cascone, P.: UrbanNext. African Fabbers Lab: Urban Ecologies, Self-Construction & Digital Fabrication|UrbanNext (2022). <https://urbannext.net/african-fabbers-lab/>
- Chaunier, L., Guessasma, S., Belhabib, S., della Valle, G., Lourdin, D., Leroy, E.: Material extrusion of plant biopolymers: opportunities & challenges for 3D Printing. *Additive Manuf.* **21**, 220–233 (2018)
- Ching, N.T., Ghobakhloo, M., Iranmanesh, M., Maroufkhani, P., Asadi, S.: Industry 4.0 applications for sustainable manufacturing: a systematic literature review and a roadmap to sustainable development. *J. Cleaner Prod.* **334**, 130133 (2022)
- Craveiro, F., Bártolo, H.M., Gale, A., Duarte, J.P., Bártolo, P.J.: A design tool for resource-efficient fabrication of 3D-graded structural building components using additive manufacturing. *Autom. Constr.* **82**, 75–83 (2017)
- Craveiro, F., Duarte, J.P., Bártolo, H.M., Bártolo, J.P.: Additive manufacturing as an enabling technology for digital construction: a perspective on construction 4.0. *Addit. Manuf.* **103**, 251–267 (2019)
- Culot, G., Nassimbeni, G., Orzes, G., Sartor, M.: Behind the definition of Industry 4.0: analysis and open questions. *Int. J. Prod. Econ.* **226**, 107617 (2020)
- Dallasega, P., Rauch, E., Linder, C.: Industry 4.0 as an enabler of proximity for construction supply chains: a systematic literature review. *Comput. Ind.* **99**, 205–225 (2018)
- Davila Delgado, J.M., et al.: Robotics and automated systems in construction: understanding industry-specific challenges for adoption. *J. Build. Eng.* **26**, 100868 (2019)
- Demissie, H.T.: 3D: Printing Africa's Development (2017)
- Design Indaba: Merging architecture, entrepreneurship and digital fabrication in Cameroon|Design Indaba (2022)
- Faksawat, K., Limsuwan, P., Naemchanthara, K.: 3D printing technique of specific bone shape based on raw clay using hydroxyapatite as an additive material. *Appl. Clay Sci.* **214**, 106269 (2021)

- Future Architecture Platform: African Fabbers Factory [AFF]: Future Architecture (2022). <https://futurearchitectureplatform.org/projects/09db0b6e-1182-47f3-bac1-4f1d7fbbef01/>
- Gadzala, A.: 3D Printing: Shaping Africa's Future (2018)
- Gershenfeld, N.: How to make almost anything. *Digital Fabrication Revolution* **91**(6), 43–57 (2012). Foreign Affairs, New York
- Guimarães, A.S., Delgado, P.Q., Lucas, S.S.: Advanced manufacturing in civil engineering. *Energies* **14**(15), 4474 (2021)
- Hadji, F., Ihaddadene, N., Ihaddadene, R., Betga, A., Charick, A., Logerais, P.O.: Thermal conductivity of two kinds of earthen building materials formerly used in Algeria. *J. Build. Eng.* **32**, 101823 (2020)
- Kidwell, J.: Best practices and applications of 3D printing in the construction industry. *Construction Management* (2017)
- Kolade, O., Adegbile, A., Sarpong, D.: Can university-industry-government collaboration drive a 3-D printing revolution in Africa? A triple helix model of technological leapfrogging in advanced manufacturing. *Technol. Soc.* **69**, 101960 (2022)
- Koutous, A., Hilali, E.: Reinforcing rammed earth with plant fibers: a case study. *Case Stud. Constr. Mater.* **14**, e00514 (2021)
- Lamrani, M., Mansour, M., Laaroussi, N., Khalfaoui, M.: Thermal study of clay bricks reinforced by three ecological materials in south of morocco. *Energy Procedia* **156**, 273–277 (2019)
- Leyronas, S.: How fab labs help meet digital challenges in Africa (2018). <https://theconversation.com/how-fab-labs-help-meet-digital-challenges-in-africa-99202>
- Manikandan, K., Jiang, X., Singh, A.A., Li, B., Qin, H.: Effects of nozzle geometries on 3D printing of clay constructs: quantifying contour deviation and mechanical properties. *Procedia Manuf.* **48**, 678–683 (2020)
- Mansouri, S., Triki, L., Zeghichi, S.: Sustainable building materials and technologies of stabilized earth. *Mod. Environ. Sci. Eng.* **3**(5), 355–363 (2017)
- Maskuriy, R., Selamat, A., Ali, K.N., Maresova, P., Krejcar, O.: Industry 4.0 for the construction industry—how ready is the industry? *Appl. Sci.* **9**(14), 2819 (2019)
- McKinsey & Company: The next normal in construction (2020). <https://www.mckinsey.com/~media/McKinsey/Industries/Capital%20Projects%20and%20Infrastructure/Our%20Insights/The%20next%20normal%20in%20construction/The-next-normal-in-construction.pdf>
- Mélanie, W.: Be More 3D conçoit une première maison imprimée en 3D en Afrique - 3Dnatives. 3Dnatives, 10 October 2019. <https://www.3dnatives.com/maison-imprimee-en-3d-en-afrique-101020193/#!>
- Millogo, Y., Morel, J.C., Aubert, J.E., Ghavami, K.: Experimental analysis of Pressed Adobe Blocks reinforced with Hibiscus cannabinus fibers. *Constr. Build. Mater.* **52**, 71–78 (2014)
- Muhammad Salman, N., Ma, G., Ijaz, N., Wang, L.: Importance and potential of cellulosic materials and derivatives in extrusion-based 3D concrete printing (3DCP): Prospects and challenges. *Constr. Build. Mater.* **291**, 123281 (2021)
- Oladele-Emmanuel, B.D., Rejeb, H.B., Redlich, T.: Strategic management: SWOT analysis of the African digital fabrication laboratories. In: 2018 IEEE International Conference on Engineering, Technology and Innovation Proceedings (2018)
- Ouakarrouch, M., el Azhary, K., Mansour, M., Laaroussi, N., Garoum, M.: Thermal study of clay bricks reinforced by sisal-fibers used in construction in South of Morocco. *Energy Rep.* **6**, 81–88 (2020)
- Parlato, M., Porto, S.M.C., Cascone, G.: Raw earth-based building materials: an investigation on mechanical properties of Florida soil-based adobes. *J. Agric. Eng.* **52**(2), 1154 (2021)
- Raji, R.: Additive manufacturing: Implications for African economies. How We Made It in Africa, 25 October 2017. <https://www.howwemadeitinafrica.com/additive-manufacturing-implications-african-economies/60103/>

- Ramakrishnan, S., Loganayagan, S., Kowshika, G., Ramprakash, C., Aruneshwaran, M.: Adobe blocks reinforced with natural fibres: a review. *Mater. Today: Proc.* **45**, 6493–6499 (2021)
- Stanislas, T.T., et al.: Effect of cellulose pulp fibres on the physical, mechanical, and thermal performance of extruded earth-based materials. *J. Build. Eng.* **39**, 102259 (2021)
- Suiker, A.S.J.: Effect of accelerated curing and layer deformations on structural failure during extrusion-based 3D Printing. *Cem. Concr. Res.* **151**, 106586 (2022)
- Suiker, A.S.J., Wolfs, R.J.M., Lucas, S.M., Salet, T.A.M.: Elastic buckling and plastic collapse during 3D concrete printing. *Cem. Concr. Res.* **135**, 106016 (2020)
- Thawer, I.: African urbanization is being transformed by 3D Printing. *Inhabitat*, 19 October 2021. <https://inhabitat.com/african-urbanization-is-being-transformed-by-3d-printing/>
- UNESCO: Ksar of Ait-Ben-Haddou - UNESCO World Heritage Centre (2021). <https://whc.unesco.org/en/list/444>
- Veliz Reyes, A., Jabi, W., Gomaa, M., Chatzivasileiadi, A., Ahmad, L., Wardhana, N.M.: Negotiated matter: a robotic exploration of craft-driven innovation. *Archit. Sci. Rev.* **62**(5), 398–408 (2019)
- Wang, Y., Han, Q., de Vries, B., Zuo, J.: How the public reacts to social impacts in construction projects? A structural equation modeling study (2016)
- Wu, P., Wang, J., Wang, X.: A critical review of the use of 3-D printing in the construction industry. *Autom. Constr.* **68**, 21–31 (2016)
- Yang, S., Wi, S., Park, J.H., Cho, H.M., Kim, S.: Novel proposal to overcome insulation limitations due to nonlinear structures using 3D printing: hybrid heat-storage system. *Energy Build.* **197**, 177–187 (2019)
- Zhang, K., Lu, B., Wang, Y., Lei, Z., Yang, Z.: Experimental strength of earth-based construction materials in different regions of China. *Adv. Mater. Sci. Eng.* **2019**, 1–9 (2019)



A Model to Evaluate the Sustainability of Buildings Within Urban Environments

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Abstract. Climate change is accelerating extreme events, rising sea levels, causing wildfires and floods, as well intensifying greenhouse and pollution effects in urban environments. Human action is a significant contributor to this extreme weather. In Brazil, most large urban areas are characterized by social exclusion, exploitation, and chaotic territory occupation, so there is a need for mechanisms promoting cultural diversity and inclusion. A sustainability assessment for buildings is critical, assuming that criteria is needed to properly embed sustainability in the built environment. A brief overview is conducted on existing evaluation methods, certificates, and stamps, and a new method is proposed, the ESA Model for Buildings (ESA-B), where sustainability is evaluated through the building life cycle regarding economic, social, and environmental aspects. This model considers the nearby urban area where the building is inserted, the strategies/practices used, as well the performance within the urban context, reflecting a dynamic relationship between the building and its surroundings.

Keywords: Sustainable buildings · Sustainability assessment · Sustainability

1 Introduction

1.1 Contextualization

Climate change is triggering extreme events. There is an increase in wildfires, floods, average temperatures, greenhouse effect, among other problems. At the root of this is human action. Society strives to propose solutions and technologies to overcome or minimize these phenomena. Such solutions demand professional action from various areas and fields of knowledge. Sustainability is evolving as a new area of knowledge, inter and multidisciplinary. A complex science to solve a wicked problem¹, difficult to define and unpredictable to solve. Let us consider today's concept of sustainability.

¹ Wicked problem: a problem whose social complexity means that it has no determinable stopping point (Tonkwise 2006).

Which variables might define it completely? The most widespread concept of sustainability is composed of three dimensions: economic, social and environmental. However, other definitions also consider cultural, institutional, religious, technical, and spiritual dimensions. On the subject of sustainability indicators, there is a great diversity, such as happiness, well-being, life quality, creativity, among others can be considered.

The most acknowledged definition proposed by the Brundtland Commission, also named *Our Common Future* (Brundtland 1987), sustainable development will be accomplished when the present generation meets its current needs “without compromising the ability of future generations to meet their own needs”. From a critical point of view, this concept needs to be satisfactory, as it is not even possible to satisfy the current generation needs with equity and justice; what about the needs of future generations?

Adopting a holistic approach to a sustainable environment implies beautiful green ecosystems, rich in biodiversity, fauna, and flora, with an abundance of water and resources, usually with no human occupation or, at most, with small communities. However, the global development scenario evolves in the opposite direction. Currently, we live in a mix of Cornucopian and Malthusian scenarios, either by replacing scarce resources with innovative technologies or with a complete scarcity of resources to feed the population, causing scenarios of misery, mortality, and extreme poverty.

Sustainability challenges are strongly related to the chaotic urban scenario, where resources and technology are needed to solve infrastructure, community living spaces, and food production problems, ideally with social development and reduced environmental impacts. Solutions are always interdependent, requiring more and more proper strategy and monitoring.

The Brazilian housing deficit rose from 5,593,191 in 2007 to 5,409,210 in 2011, according to data from Technical Note n. 1 of the IPEA. This deficit was calculated using the methodology of João Pinheiro Foundation (FJP) and data from PNAD (Furtado et al. 2013). In 2015 (FJP 2018), over 4 years (2016–2019), the deficit values reached 6,355,743 homes (in urban and rural areas), and other surveys point out values reaching 7.7 million homes (CBIC 2021). The traditional construction systems widely used in Brazil have a high environmental impact and very few professionals apply any method for selecting eco-friendly technology and low environmental impact materials in their projects. So, to eliminate the deficit of houses using the traditional construction system with less environmental impact, it is necessary to change construction technologies, materials, and Brazilian social housing.

1.2 Problematic

The real urban scenarios of major centers in Brazil are characterized by social exclusion, exploitation, and uncontrolled territory occupation. Inefficient public management makes it difficult to plan and preserve existing natural resources. Environmental priorities are often overlooked to favor personal interests.

The mechanisms to implement a building in an urban space must not only foresee problems but also sustain social cultural diversity, by valuing people’s needs, habits and culture, this way help reducing inequalities and promoting community development.

The urban spread should be made with the least impact on natural resources, a basic premise for sustainable urban development. However, urban management is such

a complex theme that it is necessary to limit the aspects to be addressed and prioritize variables to evaluate sustainability.

The urban insertion of buildings requires considering a complex range of subjects in a regional context. The smaller the scale, the greater the detail to be investigated, elucidating hypotheses to finally understand the object of study. It is also of interest the relationship between buildings and public spaces, the composition of the collective life, the spaces for circulation and living, the wealth and plurality of urban spaces. The built environment is also a space for confronting interests, which leads to evolution in the paradox of individual rights versus collective rights.

The evaluation of how green a city is can be done in several ways, from rankings designed for marketing or even to attract popular attention. In general, they are based on indicators for public health, ecology, city planning and economy. It can be argued that environmental recognition instruments, sustainability stamps and certifications can highlight some aspects of the whole. However, an instrument is needed to help addressing both the quality of public spaces and the performance of adopted strategies in a building. More than just a collection of clean technologies, sustainable building should consider the best technological strategy to supply and sustain the needs of each context. Thus, a building cannot be sustainable alone, nor a city without adequate buildings, the premise leading this research. There are best solutions for each context acquired via proper planning. The urban ambiance is not static but dynamic; it must be managed over the years.

To ensure a sustainable urban environment, not only building typology matters, but also its construction system and incorporated technologies. There is a key question guiding this research to assess building sustainability:

- How can buildings contribute to a sustainability city? How can an individual building contribute to the quality of an urban space?

This work proposes an ESA-B model, based on ESA MODEL (Librelotto 2005), to evaluate building sustainability in economic, social and environmental dimensions, considering its integration in the urban environment, an ESA MODEL for buildings named ESA-B. To assess sustainability levels, it is necessary to know what and how to measure it, involving the conceptual definition of sustainable building and sustainable city.

How to measure implies the adoption of indicators. Performance measurement in construction requires continuous improvement, changing the reality of both the building sector and the urban environment, an instrument to manage the city and reduce its environmental, economic, and social impacts.

This research proposes the ESA-B model, based on two systematic reviews, conducted by López et al. (2019) and Haapio and Viitaniemi (2008). These works identified 101 tools for sustainable building assessment, proposing a classification, which assisted in differentiating ESA-B model from other tools. A literature review was also carried out to understand the main concepts, such as the context of sustainability in Brazilian buildings, the characterization of sustainable buildings and cities, sustainability indicators, tool classification for sustainability assessment.

The most relevant aspects of the literature review are presented below in state of the art. A brief description of the ESA-b Model and its origins is given. Next, the ESA-B

Model and the main differences concerning other tools are presented as a result of this research.

This research work proposes the ESA-B model, based on two systematic reviews, conducted by López et al. (2019) and Haapio and Viitaniemi (2008). These works identified 101 tools for sustainable building assessment, proposing a classification, which assisted in differentiating ESA-B model from other tools. A literature review was also carried out to understand the main concepts, such as the context of sustainability in Brazilian buildings, the characterization of sustainable buildings and cities, sustainability indicators, tool classification for sustainability assessment.

2 State-of-the-Art

2.1 The Concept of Sustainability in the Built Environment

What is a sustainable/green city concept? According to Birch and Wachter (2008), an ideal green city through a carbon-free and completely sustainable urban space. Birch and Wachter (2008) made a distinction between managing existing spaces by adapting and mitigating unfavorable environmental conditions or developing new spaces by co-creating innovative spaces for communities. This way, to find what is a sustainable city, it is necessary to identify what would be sustainable for a specific location, the region, state, or country. Usually, sustainability is considered from the global to the local, following the example of Agendas 21 and 30, which is extended to countries, municipalities and regions, and/or specific sectors.

What is a sustainable building? There are several definitions, though the minimum premise is the balance between the economic, social and environmental dimensions, the ESA triad. The International Council for Construction (ICB) and the Agenda 21 for Sustainable Construction in Developing Countries defined key objectives for sustainable construction: i) the economy of energy and water; ii) guaranteeing the salubrity of buildings; iii) the maximization of the durability of buildings; iv) the planning of conservation and maintenance of buildings; v) the use of eco-efficient materials; vi) the employment of low construction mass; viii) a lower production of waste; and, ix) lower life cycle costs and hygiene and safety in construction works.

Following this conceptual framework, stamps and certifications establish indicators to evaluate a sustainable building, it can be considered many aspects of sustainability or less. In summary, grouping the main stamps, certificates and assessment methods (LEED, SUSTENTAX, ASUS, STAR, MASP-HIS, GB Tool, Blue House Stamp - Selo Casa Azul, Healthy House Stamp), what to expect from sustainable building, a consensus can be established between the different assessment proposals. (Silva 2007; Carvalho 2009; ASUS 2015). These proposals can serve as a basis for proposing groups of indicators for building sustainability.

On the other hand, in an urban context, Birch and Wachter (2008) identify some ways of measuring sustainability. The indicators are important to preserve natural environments, consume regional products, use electric energy from renewable sources, encourage local organic production, support educational and environmental research institutions, motivate the use of reusable packaging in restaurants and fast foods, promote parks

and activities allowing greater contact with nature, support alternative transportation and decentralizing activities in urban centers.

Other indicators can also be used for urban sustainability assessment, such as HDI - Human Development Index (PNUD 2015), the IQVU proposition - Índice de Qualidade de Vida Urbana (Nahas 2016) and the ecological footprint of Brazil, calculated by Lin (2018). These indicators can be used to propose groups of indicators for the urban structure, as well estimate impacts of climatic change over urban environments. These indicators can also be associated to evaluate sustainable environments.

Another kind of evaluation can be directed to measure a company's performance in the construction industry. This is the case of the ESA Model, proposed by Librelotto (2005), adapted from ECP-T (Abreu 2002), accordant to the proposal of Scherer and Ross (1990) and the Triple Bottom Line by Elkington (1998). This ESA Model was applied to several Brazilian construction companies by Araldi (2010), Silva (2010), as well in others industrial sectors (Carneiro 2012).

In 2017, Librelotto et al. adapted the ESA Model to assess the sustainability of buildings inserted in the urban environment, creating the ESA Model for Buildings (ESA-B Model). This assessment of was carried out by adapting the original ESA Model and defining some limits for this evaluation to make it possible to measure. Similarly, it was also considered this model with an open structure, where the indicators used can be adapted according to data availability and priorities determined for each context.

The ESA Model for Building proposes evaluate of the urban structure, conducts (practices/strategies) and of building performance. The Structure evaluation is carried out whenever the structural conditions of the building implementation place change through the incidence of Shocks, the practices (conducts) are the strategies implemented in the building, represented by the indicators identified in the stamps, certifications and models of building sustainability assessment and the Performance evaluation is the result obtained with the strategy implementation.

2.2 The ESA Model for Building (ESA-B)

It is important to emphasize that the ESA-B model is dynamic. This model allows the management of building sustainability integrated into an urban environment. The assessment of a building's sustainability level can be performed at various stages. At an early stage, to explore the viability of the venture in the project itself, or even in existing buildings. Thus, the assessment is truly dynamic, allowing to manage the neighborhood's development, monitoring the implementation of building strategies or comparing between real and planned project performance.

Figure 1 summarizes the framework of the ESA-B Model. Some indicators previously established for the urban structure can be considered for urban structure assessment, such as the existence of leisure areas in parks, public lighting conditions and sidewalks, mobility in the neighborhood, availability of electricity and water systems. It is also possible to analyze the viability of the construction, to verify the existing capacity of the local structure to meet new demands from new units, like more vehicles circulating in the neighborhood, local commerce conditions to meet new residents. These data will serve as a guide for the improvement implementation in the neighborhood, or even defining the strategies (practices) used in the building. A place where there is

a constant lack of water in public system, for instance, is an indicator that the public water network needs overhauling, which can be an agreement with the government. If that is not possible, so the building must use water management strategies (rainwater reuse, water treatment options, creation of retention basins or lakes, use of water-saving devices) to make the venture viable. In this way, the designer can prioritize the most necessary strategies to address local deficiencies or generate a greater impact on the community, avoiding technological collections or sustainability kits. Wrongly, whenever the words “sustainable building” are used, the idea of implementing the same package of technologies, like garden roofs, rainwater reuse, and photovoltaic panels often arises.

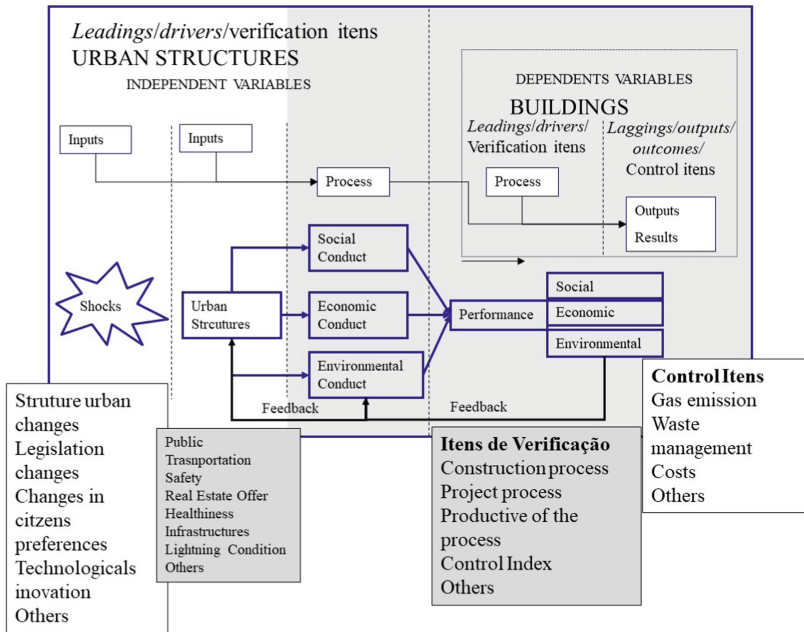


Fig. 1. ESA model for buildings’ framework (adapted from Librelotto et al. 2017).

Theoretically, the more practices are implemented in the building, the better for the planet. It is imperative to know the performance of the implemented strategies and check the balance with economic issues (initial cost, maintenance cost, local supplier availability, conditions for users to effectively manage technology), to successfully implement technology.

Once the urban structure of the building site is evaluated, further evaluations will only be conducted when shocks (changes that may modify the conditions of the neighborhood) occur. The construction of the building can be a changing agent, since it improves neighborhood conditions by offering community services, such as public leisure area, community gardens, or even providing self-generated clean energy.

A crucial issue to solve is ensuring the effectiveness of implemented technologies. Several efficient technologies, when installed in buildings, end up being ineffective, which can be harmful in terms of consumer perception and diffusion of the technology,

potentially the image of damaging of designers and consultants who recommended it. There are also cases of certified companies that use a number of strategies to achieve high certification score levels and receive credits, though buildings do not achieve the expected performance. Some cases have led to lawsuits, which got widespread media coverage.

Performance can be monitored when buildings are already in place. Strategies used for energy efficiency should revert to energy consumption savings. In this case, simulations results can be compared with the actual results. Similarly, it can be established a comparison between the use of thermal insulating materials and the internal temperature, natural ventilation with internal health conditions and temperature and so on.

3 Results

There are many ways to classify sustainable assessment tools. The Athena classification divides the methods for sustainable assessment in three levels: (i) tools for comparing products and sources of information; (ii) design of whole buildings and decision-making support tools; and (iii) assessment frameworks or systems for whole buildings. The IEA classified the methods into five categories: (i) Energy modeling software; (ii) Environmental LCA tools for buildings and building stocks; (iii) Environmental assessment frameworks and rating systems; (iv) Environmental guidelines or checklists for design and management of buildings; and (v) Environmental product declarations, catalogs, reference information, certifications and labels. López et al. (2019) propose three groups for this classification, following the steps of the Public Environmental Management Agency of the Basque Government, which are as follows: Building Sustainability Assessment Systems; Sustainable Building Standards and Assessment Tool (Carneiro 2012; Carvalho 2009).

However, evaluating sustainable buildings is very difficult as it is complex. Several indicators are considered, and many levels can be added according to the life cycle phase. None of them uses the urban development either as a parameter of control for implementing strategies in the building, or as a way to define how strategy is important and monitor its performance for management.

López et al. (2019) point out more than 600 tools to apply in sustainable building assessment and investigated 101 of these tools, identifying and defining four variables and the percentage (%) of tools, including them: i) phase of the life cycle (production of building materials, construction, use (97%) and operation, demolition (26%) and design; ii) environmental, social e economics aspects (few tools considerer all aspects of sustainability); iii) assessment categories considered (identified 10 categories - (C1) Site and sustainable development, (C2) Water, (C3) Materials and resource consumption, (C4) Energy.

The main difference between the ESA-B Model and the methods evaluated by López et al. (2019) is the importance of the urban structure as a measure for defining the strategy to be implemented in the building. Even in the category (C1) related to the site and sustainable development, the evaluation strategy adopted by the abovementioned tools is static, not allowing the integration of urban management and building sustainability.

The ESA-B model allows the definition of priorities for strategy insertion in the building and, at the same time, to monitor the performance. Similarly, building performance can be evaluated in three different moments: during design (by simulation), during use (by water consumption and energy efficiency, for example), or by user satisfaction with the performance of a given technology implemented in the building. Effective user participation in the evaluation is one of the shortcomings of these tools. Despite the proliferation of tools to evaluate building sustainability, the goal of sustainability is not easy to achieve.

4 Conclusions

A brief description of the ESA-B Model and its origins is presented in this work. This model follows the premise that building cannot be sustainable without considering its neighborhood. Even if the building use technologies for sustainability, the structure of the place is an important indicator of sustainable buildings, and the urban structure must also be considered.

To evaluate the sustainability of a building through the ESA-B Model, it is necessary to analyze the structure of the place where the building will be built. Sustainability cannot be achieved by a kit of technologies or a collection of strategies. It is necessary that place conditions guide the priorities for action. It is not possible to insert a building that claims to be sustainable in a city or a place with no infrastructure for mobility, sanitation, or quality of life. It is necessary to measure the building's contribution to the place or vice-versa. A new assessment of the location will take place whenever there is a change affecting neighborhood conditions.

The strategies used in the building are evaluated, as well building performance will be assessed and monitored after its occupancy. This way, it will be possible to determine the level of sustainability achieved by a building, which also depends on the conditions of the implementation place.

The application of the ESA-B Model as an open model allows using established databases, which can greatly simplify building assessment and monitoring. The proposed model can serve as a basis for building sustainability management.

The proposed ESA-B Model is an academic model, with only a few applications in real-life situations. This model is not only a collection of indicators but also an open system whose indicators can receive contributions from other tools, at the building level or the city one.

References

- Abreu, M.C.S.: Modelo de Avaliação da Estratégia Ambiental: Uma Ferramenta para a Tomada de Decisão (Doctoral dissertation). Programa de Pós-graduação em Engenharia de Produção, Universidade Federal de Santa Catarina, Florianópolis (2002)
- Araldi, J.: Diretrizes para a definição de ações estratégicas para tornar uma empresa da construção civil sustentável sob o aspecto econômico, social e ambiental (ESA). PPGEP. UPF (2010)
- ASUS: Sustainability assessment tool (2015). <http://asus.lpp.ufes.br/instrucoes>

- Birch, E.L., Wachter, S.M.: *Growing Greener Cities. Urban Sustainability in the Twenty-First Century. Emerging City Labels—A Global Overview*. University of Pennsylvania Press, Philadelphia, Pennsylvania (2008)
- Brundtland, G.H.: Our common future—call for action. *Environ. Conserv.* **14**(4), 291–294 (1987)
- Câmara brasileira da indústria da construção (CBIC): *Déficit habitacional no Brasil*. Disponível em (2021). <http://www.cbicdados.com.br/menu/deficit-habitacional/deficit-habitacional-no-brasil>
- Carneiro, C.: *Avaliação da sustentabilidade de uma empresa de mineração e calcinação no centro oeste de Minas Gerais: estudo de caso (Master's thesis)*. Mestrado em Engenharia Ambiental. UFSC. Florianópolis (2012)
- Carvalho, M.G.: *Metodologia para avaliação da Sustentabilidade da Habitação de Interesse Social com foco no projeto (Doctoral dissertation)*. Programa de Pós-graduação em Estruturas e Construção Civil— PECC. Departamento de Engenharia Civil e Ambiental. Universidade de Brasília, Brasília (2009)
- Elkington, J.: Partnerships from cannibals with forks: the triple bottom line of 21st-century business. *Environ. Qual. Manage.* **8**(1), 37–51 (1998)
- Fundação João Pinheiro (FJP): *Déficit habitacional no Brasil 2015*. Diretoria de estatística e informações. Belo Horizonte (2018)
- Furtado, B.A., Lima Neto, V.C., Krause, C.: *Estimativas do défice habitacional brasileiro (2007–2011) por municípios (2010)*. Brasília, DF: IPEA (2013)
- Haapio, A., Viitaniemi, P.: A critical review of building environmental assessment tools. *Environ. Impact Assess. Rev.* **28**(7), 469–482 (2008)
- Librelotto, L.I.: *Modelo ESA para avaliação da sustentabilidade na construção civil (Doctoral dissertation)*. Pós-graduação em Engenharia de Produção da Universidade Federal de Santa Catarina, Florianópolis (2005)
- Librelotto, L.I., Ferroli, P.C.M., Sanon, S., Matanna, L.: *Avaliação da Sustentabilidade do edifício na Escala Urbana*. In: *Anais ENSUS 2017-V Encontro de Sustentabilidade em Projeto*, pp. 163–177. UFSC/Virtuhab, Florianópolis (2017)
- Lin, D., et al.: Ecological footprint accounting for countries: updates and results of the national footprint accounts, 2012–2018. *Resources* **7**(3), 58 (2018)
- López, C.D., Carpio, M., Martín-Morales, M., Zamorano, M.: A comparative analysis of sustainable building assessment methods. *Sustain. Cities Soc.* **49**, 10161 (2019)
- Nahas, P., Pereira, M., Esteves, G.E.: *Metodologia de construção do índice de qualidade de vida urbana dos municípios brasileiros (IQVU-BR)*, Anais, pp. 1–20 (2016)
- Programa das Nações Unidas para o Desenvolvimento (PNUD). *Relatório do Desenvolvimento Humano 2015: o trabalho como motor do desenvolvimento humano*, New York (2015)
- Scherer, F.M., Ross, D.: *Industrial market structure and economic performance*. University of Illinois at Urbana-Champaign's Academy for entrepreneurial leadership historical research reference in entrepreneurship (1990)
- Silva, F.C.: *Avaliação da Sustentabilidade em Empresas de Construção Civil, Setor de Edificações: Estudo de Caso (Master's thesis)*. Programa de Pós-graduação em Engenharia Civil. UFSC, Florianópolis (2010)
- Silva, V.G.: *Methodologies for environmental performance assessment of buildings: current state and methodological discussion*. São Paulo, USP, Project “Technology for more sustainable housing construction”. Finep Project 2,386/04. Most sustainable housing series (2007)
- Tonkwise, C., Lorber-Kasunic, J.: What things know: exhibiting animism as artefact-based design research. *Working Papers in Art and Design*, vol. 4, pp. 1–14 (2006)



An Optically Approachable Chamber for Determining the Characteristics of Combustion of Process, Hydrogen Mixed and Natural Gases on a Near-Industrial Scale

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Abstract. This contribution presents a novel pilot plant for advanced combustion research to address current issues related to the conversion from conventional to renewable fuels. It consists of an optically accessible combustion chamber and a Nd:YAG-Dye-Laser-System, which allows a wide range of measurements within the flame, e.g. distribution of NO/OH/CH species by LIF as well as Raman and Rayleigh radiation measurements. The modularly designed combustion chamber consists of four replaceable segments and therefore is a versatile system for investigation of specific flame parameters. Gas-burners up to 50 kW fuel power can be installed, supplied by gas mixtures of up to six components and oxidants with variable oxygen content. Flue-gas recirculation is implemented as well as a staged air inlet. 18 optical windows and an axial adjustable burner guarantee a high-resolution flame examination with radial and axial profiles over the whole flame volume. In experiments with natural gas it could be shown that the deviation between the gas temperature and the wall temperature is less than 70 K. Additionally, it was also possible to precisely reproduce a previously defined target in terms of temperature, equivalence ratio and heating rate.

Keywords: Pilot plant scale · External recirculation · Wall conditions · Optically accessible combustion chamber

1 Introduction

The production [1] and use [2] of hydrogen is becoming an increasingly appealing option for the industrial sector. In addition, the fundamentals of hydrogen combustion have been extensively investigated in model flames [3–5]. Due to increasing requirements in combustion technology, multi-stage combustion systems are increasingly used in industry. In terms of changing gas qualities, e.g. the use of hydrogen and simultaneous efforts to reduce pollutants with the focus on minimizing nitrogen oxide, knowledge of the processes in large scale combustion systems becomes more and more relevant in order to optimize the burners in those systems. The pilot plant scale combustion chamber will enable the chair of “Gas and Heat Technology” to obtain high-quality experimental data

from flames. It features equipment to recirculate exhaust gases externally, equipment to use different fuel gas and oxidizer mixtures and to set and control wall temperatures. With over 15 optical ports, 24 physical access points for gas sampling allows to investigate numerous correlations.

The combustion chamber is designed for a thermal input power of 50 kW and is equipped to enable selective fuel, oxidizer and inert gas staging. This provides the possibility for significant combustion temperatures in the combustion chamber and also provides the opportunity for a technological estimation of the combustion regulation and the thermal balancing due to a large number of measuring points. In this regard, the combustion chamber was specially developed, designed and manufactured according to these requirements. In addition to the combustion chamber with multi-stage combustion control, there is comprehensive equipment for combustion diagnostics, which is permanently mounted on the combustion chamber construction by means of traverses. Combustion diagnostics include the detection of major and minor exhaust gas species as well as the recording of the local radial gas phase temperature. In particular, when selecting the equipment, attention was paid to simultaneous detection and sufficient energy for excitation with appropriately large two-dimensional light sheets. For the investigation of distribution of NO/OH/CH species a PLIF as well as additionally Raman and Rayleigh measurements could be installed to the chamber.

The pilot plant presented in this work, will be used for combustion research and addresses current issues related to the transition from conventional to renewable fuels and associated modifications in industrial systems.

The focus of research will be:

- Investigation of different industrial scaled burners and their combustion control
- Sensor testing and calibration (Operation with various flame monitoring devices like temperature-, UV- and ionization sensors)
- Determination of flame shape and structure (e.g. flame volume and length, extinction limit) with complex combustion control (staged combustion with post-combustion region)
- Investigation of concentration distribution of species (minor and major species)

Furthermore, research will be conducted on temperature distribution (TC type S) in the reactive gas phase on real burner configurations, e.g.:

- Classical orifice mixing burners with different mixing systems (thermos-processing equipment in heat treatment)
- Burner systems with staged combustion (gas turbines, heating plants in metallurgy and ceramics)
- Burner systems with exhaust gas recirculation

Therefore, different gas compositions are possible until 50 kW thermal load:

- natural gases and biogases
- natural gas-hydrogen mixtures
- hydrogen and synthesis gases (H_2 , CO_2 , CO , N_2 , C_xH_y)

The present work gives an overview about the project and the ongoing activities. First promising results were obtained under atmospheric test conditions for heating operation and investigation of the temperature difference between wall and chamber are presented. Details of novel pilot plant design and the laser-system will be explained in more detail in the following sections.

2 Experimental and Measurement Apparatus

2.1 Exchangeable Burner Systems

The combustion chamber is a modular design of 6 modules, three of which are interchangeable. Details on each module are shown in Table 1. The combustion plant has a length of about 5 m, and a system height of about 4.5 m and a combustion chamber inner diameter of 0.35 m. A hot wall combustion chamber module can be operated up to a wall temperature of 1873 K. In addition, there is an electrically heated module for constant wall temperatures up to 1475 K. Alternatively, a cold wall module guarantees constant wall temperatures below 353 K. In addition, a narrowed section in the fixed segment B separates the chamber into a primary and secondary combustion zone for the post-combustion process. This allows staged combustion. Further, in this segment, exhaust or additional air can be injected radially in four zones via nozzles. The nozzle design is characterized by the possibility of 360° rotation along the x-axis, an individually adjustable insertion depth, as well as the interchangeability of the nozzle and thus controllable outlet velocities and flow impulses. In addition, a second recirculation of the exhaust gases via the oxidizer supply pipe or via the burner is possible. All modules are identical in outer radius and length and equipped with six optical windows, three exhaust gas-sampling positions and six temperature-measuring points. Interchangeable burner systems up to 50 kW nominal power for industrial applications can be integrated into the Segment 0. In addition, it is possible to test larger burners at partial load.

By using gas mixing units, these burners can be operated on the fuel-side with fuel mixed from up to six components (CO_2 , CO , H_2 , N_2 , NG , C_xH_y) and on the oxidator-side with a gas mixture from air, N_2 , O_2 , up to oxyfuel. The installed thermal mass flow controllers (MFCs) are listed in Table 2. This allows the production of gaseous conventional and renewable mixed fuels. The industrial scale burners are axially movable and adjustable by 300 mm. This ensures optical access to the flame over the entire length.

Table 1. Installable segments for the combustion chamber with their temperature limitations

Four modular and three locally fixed segments (constant inner diameter of 350 mm)	
Fix. Seg. 0:	Front wall, with mounting for the burner, walls with high temperature lining up to 1873 K
Seg. A:	Walls with high temperature lining up to 1873 K
Fix. Seg. B:	Exhaust gas recirculation through 4 circular arranged nozzles (variable diameters/angles)
Seg. C1:	Electrically heated wall lining with constant temperature up to 1473 K
Seg. C2:	Walls with high temperature lining up to 1673 K
Seg. D:	Double wall water cooling down to a temperature ≤ 343 K
Fix. Seg. E:	Taper 90° bend with exhaust gas heat exchanger up to 1473 K
Fix. Seg. 0:	Front wall, with mounting for the burner, walls with high temperature lining up to 1873 K

The interchangeable burner (see Fig. 1) can be integrated into the burner block combined with thermal sensor, pressure sensor and optical combustion chamber monitoring. In the current configuration, a burner type Kromschröder BIO50 (type: HB-600-535-(37)D) is installed. The swirl and the flame unit are retracted slightly into the flame tube to allow optical accessibility at the flame root. The total length of the flame tube is 600 mm while the mixing unit is placed at a position of 535 mm inside the tube. The heating process was carried out in two intervals of 14 h shifts with a break of 6 h between the two days in which the channel cooled down slightly. The load profile selected in Fig. 6 was tested. This consisted of a slow heat-up phase to 550 K in the first 5 h to allow drying of moist components (Fig. 2).

Table 2. Installed thermal mass flow meters with their sizes and uncertainties

Fuel side		
Natural gas	5 m ³ n/h	±0,8% of measured value ±0,3% of final value
Hydrogen	15 m ³ n/h	±0,5% of measured value ±0,1% of final value
Carbon monoxide	15 m ³ n/h	
Methane	5 m ³ n/h	
Carbon dioxide	10 m ³ n/h	

(continued)

Table 2. (continued)

Fuel side		
Nitrogen	10 m ³ n/h	
Liquid fuel	60 kg/h	±0,2% of measured value
Oxidizer side		
Air	60 m ³ n/h	±1,5% of measured value ±0,3% of final value
Oxygen	10 m ³ n/h	±0,5% of measured value
Nitrogen	50 m ³ n/h	±0,1% of final value

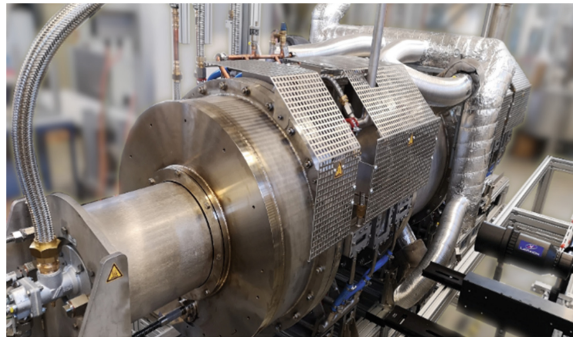


Fig. 1. View of the combustion chamber from the burner side, right: view of the optical assembly, left: view of the axially adjustable burner

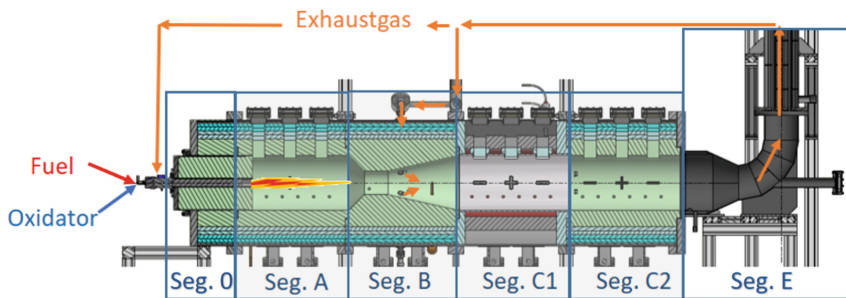


Fig. 2. Schematic structure of the optically accessible combustion chamber with the flow of the exhaust gas recirculation system

2.2 Calibration Burner

To ensure comparable values between the measurement series, the laser and camera system has to be calibrated. The McKenna calibration burner system is used for measurements in flat flames (see Fig. 3 a), exhaust gas composition via the height above the burner (HAB) and for calibration of the optical systems (LIF, Raman and Rayleigh). For LIF, the camera system, intensifier and post measurement calculation have to be calibrated. Therefore, both a beam energy correction to compensate the laser beam intensity over the height (e.g. via acetone LIF, as in Fig. 3 b) and a background subtraction, are performed. The latter is used to compensate for false light, not coming from the combustion process to be investigated. Subsequently, a defined volume fraction of reference gas can be transferred to the combustion system via mass flow controllers and conducted through the burner plate into the examination area. Here, individual radicals are excited by means of wavelengths tuned to the radicals and recorded by the camera. Thus, a correlation between reference gas composition and light intensity is possible afterwards. With the exception of the light intensity, this correlation can be used to draw conclusions about the measured concentration. This procedure is performed for several calibration points to allow a better correlation.

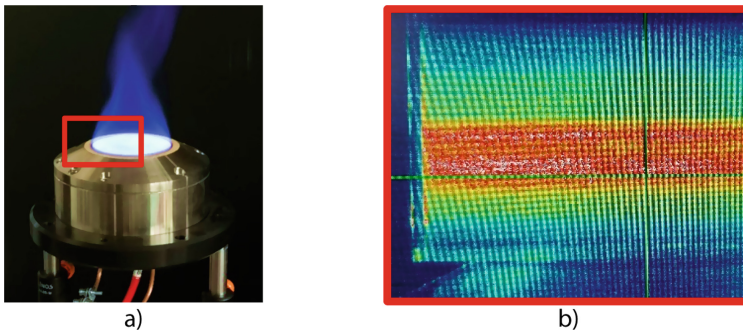


Fig. 3. a) Calibration set-up using a burner-stabilized flat flame without nitrogen co-flow on a McKenna burner under fuel-rich conditions in a methane flame, b) Acetone PLIF in a quartz glass chamber for sheet intensity correction over plate of a McKenna burner

2.3 Optical Setup

The laser beam is introduced horizontally through the quartz glass windows. A camera detects the emitted radiation vertically with optical filters and an upstream image intensifier. The detailed construction can be seen in Fig. 4 and Fig. 5. For optical evaluation, a CMOS camera system (Imager M-lite) was combined with an image light amplifier (IRO-X) to provide vertical and orthogonal images of the flame zone and the laser light section. An UV lens ($T > 90\%$) and filters for OH ($T \sim 80\%$), CH ($T \sim 90\%$), NO ($T = 80\%$) and acetone-PLIF were combined. For measurements using Raman/Rayleigh system, an imaging spectrograph could be installed. This allows the distributions of the

main species N_2 , O_2 , H_2 , CO , CO_2 , and H_2O to be studied, and subsequent calculations to determine the relative concentration and temperature fields. For the use in combination with the combustion chamber and the expected amount of infrared radiation of the chamber walls, a beam splitter was integrated. Suitable for heat radiation reduction and simultaneously OH- and CH-LIF measurements an optical semi-transparent mirror coated on both sides (R: 300–550 nm; T: 700–1400 nm) was developed. In addition, a second optical semi-transparent mirror coated system was developed for NO-PLIF measurements, which was adapted to the emission wavelength (R: approx. 240–290 nm (>80%); T: approx. 310–1500 nm (>85%)).

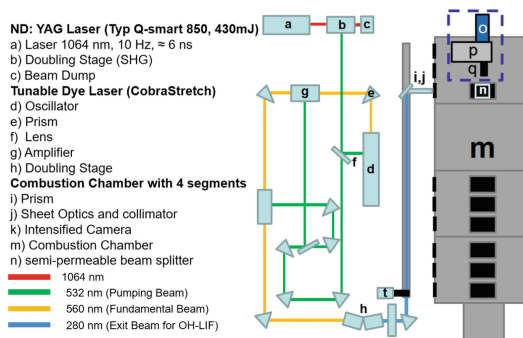


Fig. 4. Set-up for PLIF using a ND: YAG Laser (Typ Q-smart 850, 430 mJ) with a tunable Dye Laser (CobraStretch)

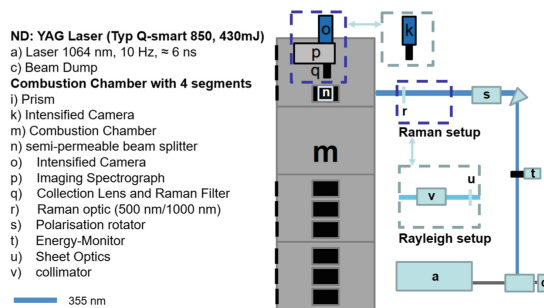


Fig. 5. Set-up for Rayleigh, Raman using a ND: YAG Laser (Typ Q-smart 850, 430 mJ) with an imaging spectrograph for ICCD camera

3 Experiments Results

The installed burner was operated and a detailed test matrix for natural gas as fuel was measured. In the first phase, heating and wall temperature distribution of all modules was of importance in order to investigate the temperature differences between the combustion chamber and the wall as a function of the operating time. With a low temperature

increase, heating to the maximum temperature was then carried out in natural gas operating mode. As expected, the maximum temperature gradient decreases in the course of the experiment (see Figs. 6 and 8). The difference between the chamber temperature and the wall temperature in chamber A dropped from approx. 220 K to around 75 K. However, it can be seen that the target air ratio ($\lambda = 1/\phi$) was met very well and there were only deviations in the shutdown processes. The maximum thermal input power for the current burner setup was 48 kW (see Fig. 7) when firing natural gas with air at $\lambda = 1.02$.

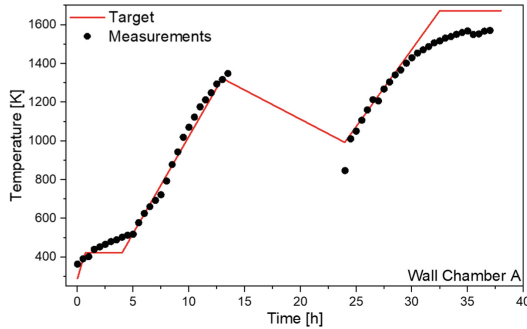


Fig. 6. Measurements of the wall temperature in comparison with the target value of the heating process

In addition, module interaction was investigated. It was found that the wall and chamber temperature behavior in all segments was similar, and no further time delay between chamber A and chamber C2 was measured. The system does responds fast to changes in the flame, indicating a sufficiently low thermal inertia.

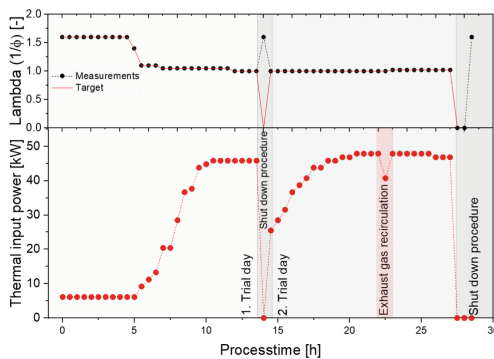


Fig. 7. Target mixing ratio of the natural gas/air mixtures with the correlating thermal burner input power during the heating process

It should be noted, that the measured values for all measuring points were recorded in an interval of 15 min. As expected, it can also be seen in Fig. 9 that the temperature

of the two thermocouples located near the flame (Seg. A and Seg. B) are significantly higher than that of the wall thermocouple in segment C1/C2.

Further it should be noted that no temperature correction for the radiation was applied to the graphs shown. In the future, a correction will be chosen using the Shaddix [6] approach, which includes both the geometry and the flow velocity in the chamber. It is worth noting that after the constriction in segment B, the temperature is significantly lower, this is attributed primarily to a lower radiative transfer from the first to the second combustion chamber.

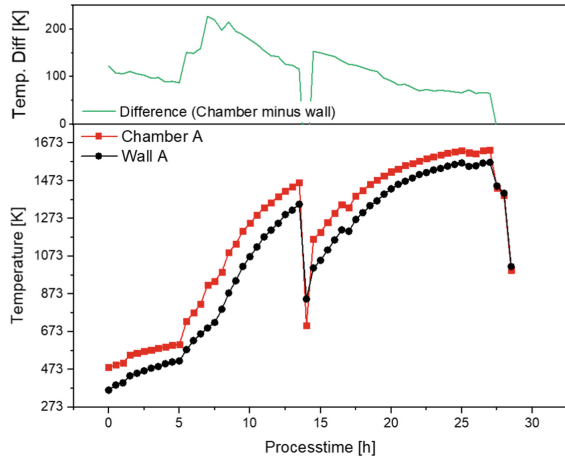


Fig. 8. Investigation of the temperature difference between the internal chamber temperature and the chamber wall temperature as a function of the process runtime

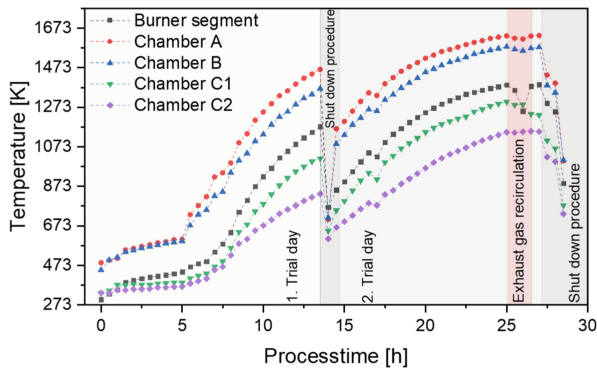


Fig. 9. Consideration of the temperature behavior of the shoring combustion chambers A to C2 as a function of the process time and the heating power shown in Fig. 7

4 Conclusions and Future Work

A new optically accessible combustion chamber was put into operation. The first extensive heating tests were carried out and the temperature distribution in the individual combustion chambers was investigated using type S thermocouples. In addition, the setup, the measurement procedure and the optical system were described in detail. Initial measurement results show that a preheating time of at least 7 h is required to get the difference between the chamber and the wall below 100 K in natural gas operation, which was also the target temperature difference of the investigation. Finally, it was shown that the maximum chamber temperature with natural gas air firing does not exceed 1673 K within a running time of 25 h. The combustion chamber is scheduled for three large industrial-and research projects. The topics range from development of burner to testing of new materials to safety investigations in combination with oxy-fuel. The first research project started in January 2021 for the development of an ultra-low-NO_x-burner operated with up to 100% H₂ with regard to safety aspects. Concepts for burner development for use in the high-temperature range with low exhaust emissions are under preparation. In addition, scale-up approaches and standardization concepts are developed according to the modular principle [7]. The second research project started in January 2021 as well, under the aspect of the further development of a material concept for partially hydrogen-fired furnaces by means of tests with hydrogen and steam atmospheres at temperatures up to 1800 K. It will enable furnace and burner manufacturers to quickly and properly identify suitable materials. At the same time, it can be determined for which furnaces a change of fuel would be problematic [8]. Visualization of flame position, flame volume, investigation of exhaust gas emissions, temperature regimes and behavior in an H₂-oxy-fuel burner for the glass industry [9].

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References

1. Dincer, I., Acar, C.: Review and evaluation of hydrogen production methods for better sustainability. *Int. J. Hydrogen Energy* **40**(34), 11094–11111 (2015)
2. Cao, X., Wei, Z.: technologies for the safe use of hydrogen and construction of the safety standards system. *Chin. J. Eng. Sci.* **22**(5), 144 (2020)
3. Sánchez, A.L., Williams, F.A.: Recent advances in understanding of flammability characteristics of hydrogen. *Prog. Energy Combust. Sci.* **41**, 1–55 (2014)
4. Miao, H., Lu, L., Huang, Z.: Flammability limits of hydrogen-enriched natural gas. *Int. J. Hydrogen Energy* **36**(11), 6937–6947 (2011)
5. Eckart, S., Pizzuti, L., Fritsche, C., Krause, H.: Experimental study and proposed power correlation for laminar burning velocity of hydrogen-diluted methane with respect to pressure and temperature variation. *Int. J. Hydrogen Energy* **47**, 6334–6348 (2022)

6. Shaddix, C. R.: A new method to compute the proper radiant heat transfer correction of bare-wire thermocouple measurements. In: Proceedings 10th U. S. National Combustion Meeting. (2017)
7. Grant notice: AiF-IGF project: ULowBurn, FK: BG07591/20 (2020)
8. Grant notice: AIF-IGF project: ResInMa, FK: FLBG07593/20 (2020)
9. Grant notice: BMBF project: MigWa, FK: 01LJ2001B (2020)



Relevant Issues in the Management of Biomass Parks in Power Generation Plants

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Abstract. Biomass is a renewable energy source that, due to its high seasonality, needs to be stored, handled and managed in suitable conditions for its optimum use. Storage is, therefore, a key process in which biomass can lose much of its qualities as fuel. The use of a good storage method will greatly reduce the economic losses associated with energy use of biomass, and storage process can be used to improve fuel quality. Furthermore, storing and handling biomass is highly dependent on the type and shape of the biomass (crushed, grinded, baled, logged, pelletized, etc.) and products are usually separated at the ground and organized by types and characteristics, especially when there is an economic or financial advantage between the products.

Supported by this background, the paper presents the results of the research developed by the University of Jaen in which storage tests have been carried out on different types of biomass (Pine, Poplar, Olive Pruning, Oil Mill Leaf, Vine Shoot, Vine Strain, Fruit Tree Pruning, Olive pomace and Olive Stone). Such biomasses are destined to electricity generation in a power plant located in southern Spain. Sixty-two tests have been carried out with different storage configurations and the evolution of the main variables within the collection (temperature, humidity and biological activity) has been monitored.

As a result of the study, it has been proposed a simple methodology that allows sustainable management of the biomass park, prioritizing the use of those piles that present risks of degradation or self-ignition.

Keywords: Biomass storage · Renewable resources · Power generation plants

1 Introduction

1.1 Biomass Storage

Biomass is a renewable energy source that, due to its high seasonality, needs to be stored, handled and managed in suitable conditions for its optimum use.

Storage is a key process in which biomass can lose much of its qualities as fuel. The use of a good storage method will greatly reduce losses [1], reducing in turn the economic losses associated with energy use of biomass.

On the other hand, other studies show that the storage of biomass in the field can be used to improve fuel quality [2] as quality of wood changes during storage and its net energy yield does. Furthermore, storing and handling biomass is highly dependent on the type and shape of the biomass (crushed, grinded, baled, logged, pelletized, etc.) and products are usually separated at the ground and organized by types and characteristics. This separation is mainly needed when there is an economic or financial advantage between the products.

Hence, any study must take into account the main characteristics of biomass: density, moisture content, particle size, cohesion, and coefficient of friction.

1.2 Main Factors Affecting Biomass Storage

The main factors affecting the quality of biomass during storage are moisture content, granulometry, stockpile size, airflow, temperature and microbial activity.

In addition, most of the studies agree that biomass moisture content is the most important characteristic as a crucial factor that generates temperature increases within the stockpile, putting at risk the quality of the biomass during storage [3-6]. If the initial humidity is high, more heat is generated inside the storage and thus the temperature rises. In addition, this temperature increase is a determining factor for internal reactions and the risk of self-ignition. The moisture content also increases the degradation caused by the action of bacteria, fungi and microorganisms, in addition to the degradation caused by chemical reactions at high temperature.

The size of the stockpiles is another critical factor. Moist biomass products should not be stored in large accumulations because, in this case, air circulation is reduced and the dissipation of the heat generated inside decreases, favouring the action of microorganisms and the self-heating of the biomass.

A correct storage method may reduce losses, degradation and self-ignition risks, and the energy quality of the fuel could be improved, taking advantage of the storage process to optimize the net energy yield.

2 Test Campaign in Southern Spain

2.1 Purpose and Facilities

In order to assess the effect of large-scale storage of biomass resources, a study has been carried out in an electricity generation plant located in southern Spain. To this end, a series of field tests have been carried out with different types of biomass resources used in the plant, observing and analysing the behaviour of these products during storage and the changes that occur in their main characteristics [7]. The research was developed by the University of Jaen testing ten different types of biomass (Pine, Poplar, Olive Pruning, Oil Mill Leaf, Vine Shoot, Vine Strain, Gardening Remains, Fruit Tree Pruning, Olive pomace).

Sixty-two tests have been carried out with different storage configurations and the evolution of the main variables within the collection (temperature, humidity and biological activity) has been monitored (Table 1).

2.2 Fieldwork an Data Collection

The power plant has more than 4 useful hectares of biomass storage and consumes nearly 120,000 tons of different types of biomass per year. With a nominal power of 16 MW, combustion takes place on a vibrating grate cooled by water and by the combustion air itself. Although this plant is designed so that its biomass consumption can be composed by 100% of olive pruning, in this plant poly-biofuel mixtures are also used.

An initial classification and differentiation among the types and sizes of stockpiles were made:

- Large stockpiles. Those that will measure more than 50 m in length, 20 m in width and more than 7 m in height.
- Medium Stockpiles. Those in which the length is between 20 - 50 m long, 10 - 20 m wide and between 4 - 7 m high.
- Small stockpiles. Stockpiles with sizes less than 20 m in length, 10 m in width and 4 m in height.

In each of the new stockpiles, the weight at the beginning of storage was recorded and random samples were taken from different parts of the material to be analysed to obtain the following parameters:

- Initial Humidity (%). Moisture analysis is carried out according to UNE-CENT/TS 14774-1/2/3, by drying the sample in oven at 105°C up to constant weight.
- Initial Higher Heating Value (HHV) (kcal/kg). The HHV is analysed by means of a PAR 6000 Calorimetric Pump according to Standard UNE-EN-14918.
- Initial Lower Heating Value (LHV) (kcal/kg). According to the HHV data obtained in the calorimetric pump and according to the UNE-EN-14918 Standard.
- Temperature control by means of a FLIR ix series Extech IRC30 Thermographic Camera.
- Temperature evolution inside the collection. By means of a temperature probe placed in the stockpile that informs of what is happening inside the collection.

2.3 Test Results

Table 2 shows a brief summary of the results obtained by product type, including statistical information on the behaviour of the different variables.

Table 1. Main characteristics of the types of biomass tested [7]

Biomass	Moisture content ¹ (%)	NHV (kcal/kg)	Bulk density (kg/m ³)	Seasonality	Leafy content	Ash content	Volatility
Pine	30–40%	3,400–3,600	200–250	Apr-Sep	Low	Low	High
Poplar	>35%	2,800–3,000	220–300	Feb-Jul	Low	Low	Medium
Olive pruning	35%	3,200–3,500	120–200	Feb-Apr	High	High	Low
Olive leaf	>40%	2,600–2,900	N/A	Feb-Apr	Very high	High	Low
Wine shoot	20%	2,900–3,200	200–300	Dec-Feb	Low	High	Medium
Fruit pruning	<20%	3,100–3,400	200–300	Oct-Mar	Very low	Medium	Low
Olive dry pomace	<15%	3,700–4,100	550–650	Apr-Jun	Very low	Very high	High

Table 2. Summary table of biomass storage tests performed by type of product [7]

Product	N° Tests	Mean residence time (days)	Mean initial moisture (%)	Mean final mois (%)	Mean temp (°C)	Mean initial weight (T _n)	Mean final weight (T _n)	Mean initial NHV (kcal/kg)	Mean final NHV (kcal/kg)
Pine	17	170.41	25.13%	16.86%	50.36	1,050.22	977.91	3,228.40	3,546.50
Crushed olive pruning	13	140.54	23.95%	16.90%	66.35	979.36	919.35	3,132.70	3,313.30
Olive leaf	11	087.91	32.83%	29.55%	69.54	1,345.91	1,260.42	2,809.10	2,892.00
Vine shoot	5	235.20	22.64%	13.49%	41.18	741.34	723.84	2,920.50	3,363.20
Poplar	4	211.00	29.70%	16.61%	51.08	728.33	614.07	2,878.70	3,318.70
Fruit pruning	4	294.75	16.87%	10.76%	44.5	724.53	692.94	3,503.70	3,555.10
Olive Dry Pomace	4	252.25	13.38%	11.48%	36.25	2497.98	2,496.40	4,019.10	4,065.20
Pre-crushed olive pruning	3	302.33	15.26%	11.38%	56.33	1522.09	1,383.23	3,495.90	3,653.60

3 Storage Management Model

A new storage management model has been designed, as there is a need to manage a large amount of stock composed of different biomasses that have different physical-chemical characteristics.

¹ Usual results of moisture analysis carried out according to UNE-CENT/TS 14774–1/2/3 Standard.

Methodology should be simple and should allow sustainable management of the biomass park, prioritizing the use of those stockpiles that present risks of degradation or self-ignition. The moment of the end of storage of the product will be marked by:

- Evolution and optimal status of the biomass in the stockpile during the storage period.
- Conditions and characteristics of entry at the start of storage.
- In equal conditions, FIFO (First IN – First OUT).

The proposed model considers five key factors (Moisture content, Residence time, Herbaceous component, Temperature, Stockpile size and Granulometry) for biomass management and uses, for each of them, prioritization criteria defined by experience and field tests (see example in Table 3).

Table 3. Priority criteria according to the moisture content.

Biomass type	Initial moisture content				
	5,00%	15,00%	25,00%	35,00%	45,00%
Pine	1,10	2,20	3,60	5,20	7,00
Olive Tree pruning	1,10	2,40	3,90	5,60	7,50
Olive tree leaf	1,20	2,60	4,20	6,00	7,50
Vine branches	1,10	2,20	3,60	5,20	7,00
Poplar	1,10	2,20	3,60	5,20	7,00
Fruit tree pruning	1,10	2,20	3,60	5,20	7,00
Vine trunk	1,10	2,20	3,60	5,20	7,00
Gardening residues	1,10	2,40	3,90	5,60	7,50
Dry Olive pomace	1,10	2,60	4,20	6,00	7,50

Finally, weighting values are assigned to each of the factors according to their importance in biomass degradation, and the stockpiles inside the park are then sorted according to their consumption priority. The collection with the highest consumption priority is the one with the highest score (see Figs. 1 and 2).

Puntuación de Prioridades													
IMPORTANCIA FACTOR	30,00%	15,00%	5,00%	7,00%	5,00%	38,00%	Prioridad Humedad	Prioridad Herbicéo	Prioridad Apto	Prioridad Residencia	Prioridad Tamaño	Prioridad Temperatura	100,00%
Producto	Humedad Inicial	Componente Herbéacea	Triturado / Sin Triturar	Tiempo Residencia	Tamaño Acopio	Temperatura Acopio							Prioridad Total
Orujillo	9,50%	Muy Bajo	Triturado	9,9	Muy Grande	45,00	1,10	1,10	1,00	6,00	5,50	1,10	17,46
B6. Pino	25,85%	Bajo	Triturado	12,5	Grande	50,80	3,60	2,20	2,00	7,00	5,20	2,20	25,30
B6. Clivo Trn.	22,05%	Alto	Triturado	14,5	Muy Grande	77,00	2,40	5,60	4,00	7,50	7,50	4,20	35,46
Orujillo	10,00%	Muy Bajo	Triturado	21,1	Muy Grande	65,00	1,10	1,10	1,00	6,00	5,50	4,20	21,74
B6. Clivo Prehit.	5,88%	Alto	Triturado	10,4	Pequeño	35,00	1,10	5,60	4,00	7,00	2,20	1,10	23,39
B6. Clivo Prehit.	6,44%	Alto	Sin Triturar	12,2	Muy Grande	45,00	1,10	5,60	2,00	7,00	7,00	1,10	26,33
Orujillo	11,42%	Muy Bajo	Triturado	23,3	Muy Grande	50,00	1,10	1,10	1,00	6,00	5,50	2,80	19,80
Orujillo	11,27%	Muy Bajo	Triturado	40,1	Muy Grande	60,00	1,10	1,10	1,00	6,00	5,50	2,80	19,80
B6. Clivo Prehit.	19,37%	Alto	Sin Triturar	24,7	Muy Grande	55,00	2,20	5,60	2,00	7,00	7,00	2,60	29,83
B6. Clivo Trn.	24,63%	Alto	Triturado	25,7	Mediano	48,80	2,40	5,60	4,00	7,50	4,20	1,10	27,71
B6.2 Samiento Vid Prehit.	23,40%	Bajo	Sin Triturar	24,7	Pequeño	29,00	2,20	2,20	1,00	6,50	2,20	1,10	17,22
B6. Clivo Prehit.	16,77%	Alto	Sin Triturar	24,7	Mediano	42,00	2,20	5,60	2,00	7,00	3,60	1,10	24,19
B6.2 Restos de Podas Prehit.	17,94%	Muy Bajo	Alto	24,7	Muy Pequeño	42,00	2,40	7,50	2,00	7,50	1,10	1,10	24,54
B6. Clivo Prehit.	15,98%	Alto	Sin Triturar	24,2	Mediano	48,80	2,20	5,60	2,00	7,00	3,60	1,10	24,19
B6. Clivo Prehit.	17,70%	Alto	Sin Triturar	24,0	Mediano	48,80	2,20	5,60	2,00	7,00	3,60	1,10	24,19
B6. Clivo Trn.	9,80%	Alto	Triturado	23,8	Muy Grande	53,00	1,10	5,60	4,00	7,50	7,50	2,60	31,56
B6. Clivo Prehit.	14,57%	Alto	Sin Triturar	23,0	Muy Pequeño	42,00	1,10	5,60	2,00	7,00	1,10	1,10	20,13
B6.2 Restos de Podas Prehit.	19,65%	Muy Alto	Sin Triturar	23,0	Pequeño	42,00	2,40	7,50	2,00	7,50	2,60	1,10	26,12
B6. Clivo Prehit.	16,77%	Alto	Sin Triturar	24,7	Mediano	42,00	2,20	5,60	2,00	7,00	3,60	1,10	24,19
Orujillo	10,00%	Muy Bajo	Triturado	15,0	Muy Grande	65,00	1,10	1,10	1,00	6,00	5,50	4,20	21,74
Orujillo	10,00%	Muy Bajo	Triturado	14,1	Muy Grande	50,00	1,10	1,10	1,00	6,00	5,50	2,80	19,80
B6. Clivo Trn.	10,33%	Alto	Triturado	13,1	Muy Grande	62,00	1,10	5,60	4,00	7,50	7,50	2,60	31,56

Fig. 1. Table of priorities (example).

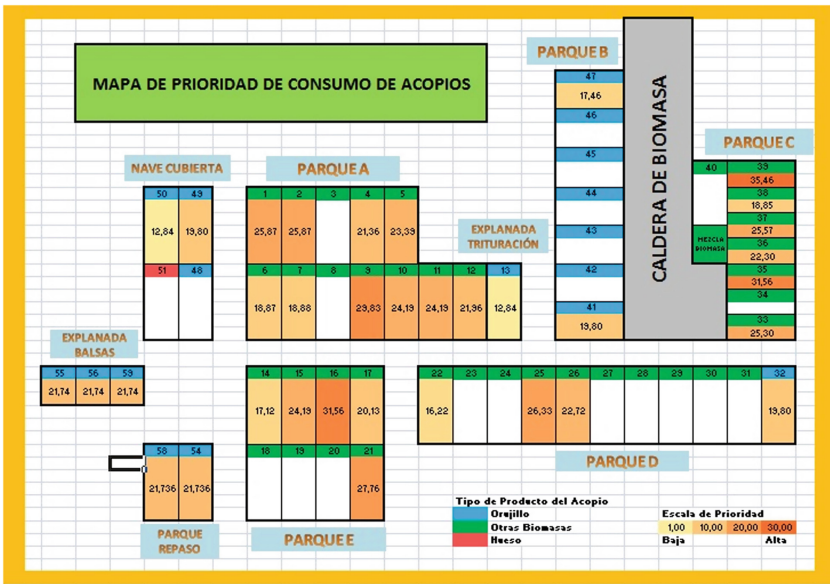


Fig. 2. Example of the Priority Map used to manage the biomass storage park.

4 Conclusions

The management of a biomass storage park, especially when multiple biomass products are used, is a key process in power generation activities. It must establish the size of the stockpiles according to the type and characteristics of the products and the piles must be monitored to analyse the evolution of the biomass during the storage time, in order to be able to consume it at the optimum time.

The proposed management model, based on extensive fieldwork, makes it possible to prioritise stockpiles in the park and optimise biomass consumption ratios, minimising the risks of degradation and self-ignition in the park.

One of the most important characteristics of this model is that it is simple to implement, and very versatile. Mainly because it is based on assigning values of importance to the main factors that influence the storage of each of the biomasses used, and can be adapted to each type of storage facility, to each biomass and to the different ways of working of each one.

References

1. Emery, I., Dunn, J.B., Han, J., Wang, M.: Biomass storage options influence net energy and emissions of cellulosic ethanol. *BioEnergy Research* **8**(2), 590–604 (2014). <https://doi.org/10.1007/s12155-014-9539-0>
2. Gautam, S., Pulkki, R., Shahi, C., Leitch, M.: Fuel quality changes in full tree logging residue during storage in roadside slash piles in Northwestern Ontario. *Biomass Bioenerg.* **42**, 43–50 (2012). <https://doi.org/10.1016/j.biombioe.2012.03.015>
3. Lara Chaves, P.J., Terrados Cepeda, J., Gallego Álvarez, F.J., Her-moso Orzáez, M.J.: Influence of Moisture, Temperature and Microbial Activity in Biomass Sustainable Storage. Special Focus on Olive Biomasses. *Int. J. Environ. Sci. Nat. Res.* **25**(2) (2020). <https://doi.org/10.19080/IJESNR.2020.25.556165>
4. IEA. Health and Safety Aspects of Solid Biomass Storage. IEA Bioenergy, May 2013
5. Ashman, J.M., Jones, J.M., Williams, A.: Some characteristics of the self-heating of the large scale storage of biomass. *Fuel Process. Technol.* **174**, 1–8 (2018). <https://doi.org/10.1016/j.fuproc.2018.02.004>
6. Sahoo, K., Mani, S.: Techno-economic assessment of biomass bales storage systems for a large-scale biorefinery. *Biofuels Bioproducts Biorefining* (2017). <https://doi.org/10.1002/bbb.1751>
7. Lara Chaves, P.J., Terrados Cepeda, J., Gallego Álvarez, F.J., Her-moso Orzáez, M.J.: Large-scale biomass storage for electricity generation: a comprehensive field-test campaign in southern Spain. *Biofuels Bioproducts Biorefining*, n/a(n/a) (2021). <https://doi.org/10.1002/bbb.2337>



Combating Climate Change with Phytoremediation. Is It Possible?

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Abstract. Soil contamination causes several environmental problems such as contamination of water resources, desertification, contamination of food crops, which, directly or indirectly, may bring health problems to humans. Therefore, there is a need to decontaminate the soils. Phytoremediation, the decontamination using plants, is an interesting alternative, especially when energy crops are adopted. Most of the energy crops are considered tolerant to contaminated soils, and the action merges the economical exploitation of the biomass for bioenergy or biomaterials, bringing additional income, with the decontamination action. Moreover, its use brings additional environmental returns, such as, the reduction of greenhouse gases and fossil energy savings, thus serving to combat climate change. In addition, phytoremediation with energy crops may bring to rural areas social benefits, and its launch on contaminated land, reduces competition for feed and food and land-use conflicts. However, the soil marginality and affect the productivity and biomass characteristics, threatening the environmental benefits and the economic value. In this context, it was reviewed the production of these crops in heavy metal contaminated soils, with a focus on the environmental aspects and the technological hindrances related with biomass quality. Ultimately, a critical evaluation of the literature data is made, and menaces and prospects are highlighted.

Keywords: Energy crops · Environmental impact assessment · Heavy metals · Socio-economic impact · Soil contamination

1 Introduction

Soil contamination, resulting from several anthropogenic activities, deserves attention due to the impacts caused to the environment [1]. Indeed, soil contamination causes threats and several environmental problems such as contamination of food crops and water resources, desertification, among others, which can, directly or indirectly, can cause health problems for humans [1–4]. Remediation of the soils will help to solve these situations, and several techniques can be applied (chemical, physical, and/or biological). The decontamination process can be done through the use of plants (phytoremediation), for example through the implementation of energy crops [2]. This option is valid, once these crops tolerate soil contamination, being able to remediate the soils, along with the production of a biomass that can be used for bioenergy or biomaterials, bringing additional revenue to farmers [3, 5–12]. Moreover, the introduction of these energy crops in contaminated soils brings environmental, namely because its use can help reducing greenhouse gases and provide fossil energy savings, in line with the climate change combating goal [13, 14]. Moreover, the establishment of energy crops on land contaminated, reduces the conflicts of land-use change once these soils are not exploited for food and feed [13, 15–17]. Several species can be grown to generate energy. Lignocellulosic crops are interesting crops. They provide high biomass production and energy content [7, 8, 18, 19]. Oil crops, rich in fatty acids, can be used to replace fossil feedstock's, namely surfactants, plastics, plasticizers, lubricants, detergents and other products, [20]. However, the soil marginality can affect the amount of biomass produced per land area and the characteristics of the biomass, with effects on the environmental savings and economic value [21, 22]. In this context, the aim of this work was to review current information on the production of energy crops in heavy metal contaminated soils, with a focus on the technological constraints and environmental gains associated with the use of a biomass harvested from contaminated land. Ultimately, a critical evaluation of the literature data is made, and menaces and prospects are highlighted.

2 Energy Balance and Potential Reduction of Greenhouse Gases Emissions

Establishing crops on contaminated land contributes to trap CO₂, consequently GHG emissions balance in a value chain can potentially be reduced when compared with fossil-based value chains. In addition, use of contaminated land for the production of biomass for biofuels, power and heat, and biobased materials, can reduce the impact associated with the use of fossil-based resources, which can reduce the fossil based energy dependence. Indeed, the use of energy crops for bioenergy, biofuels or for biobased products may help to replace or conserve fossil fuels.

Environmental performance of energy crops produced in contaminated land, in terms of reduction of greenhouse gases and energy savings, is dependent on crop yield, the amount of inputs (e.g. fertilizers, irrigation, among others), and the processing options (for energy, biomaterials, etc.) [23–26].

In each process, the energy balance can be calculated by subtracting the energy input to the potential energy produced. Also, the reduction of greenhouse gas (GHG)

emissions can be calculated by estimating the amount of carbon captured during the photosynthesis and the amount released during the cultivation, processing and use. In this evaluation, other contributing gases to GHG emissions are also accounted (e.g. N_2O and CH_4) [23, 25].

Several works involving perennial crops to bioenergy, growing in contaminated soils, indicated that the energy balance tails the yields shape, being higher, when yields are higher, and the opposite when yields are reduced due to the toxicity of the contaminated land. Yet, most of the studies indicate that the production and use of those crops for bioenergy will allow to save a significant amount of fossil energy. This was reported in the work of Gomes and collaborators [23]. In this work, the energy balance of switchgrass cultivated in contaminated soils as solid fuel in a combustion process was determined. Results show a positive energy balance in the range 154–310 GJ/ha. The same positive balance was observed with *Miscanthus* cultivated in contaminated soils as solid fuel [24]. The reduction in yields affected also negatively the energy balance in the work of Schmidt et al. [25], that tested different perennial crops (*Miscanthus*, switchgrass, giant reed and cardoon) in marginal soils of Europe. Results from this work also show that the use of these crops for heat and power production in a small CHP, present energy savings, even when biomass was cultivated in marginal soils, and that *Miscanthus* performed better, followed by giant reed, cardoon and at the end switchgrass. Schmidt et al. [25], in their work also compared the energy balance associated with different processing options. And results showed that combined heat and power production presented the best savings. Stationary heat production also presented a good balance. Second-generation ethanol, 1,3-propanediol and biochar production showed worse results. Results presented in the literature for the global energy requirement (GER) concerning industrial application of fiber crops (e.g. hemp, kenaf), show that bio-based products may require more or less GER than the non-renewable-based material, depending on the choice of this reference material [26]. For example, production of insulation board from kenaf-fibers or flax rolls consumes less energy than polyurethane and more energy than stone wool, paper wool and mineral wool [27].

Concerning the reduction of greenhouse gas (GHG) emissions, use of perennial grasses for bioenergy can save an average of 5, 18 and 36 $MgCO_2$ -eq per ha per year, when used to produce, respectively, ethanol, electricity and cogeneration, or heating generation [28], similar to sorghum (sugar crop), and higher than fiber crops. And even when crops are being cultivated in contaminated soils, literature indicates that the use of perennial crops (e.g. switchgrass) as solid fuel is relevant to reduce GHG emissions [23].

However, the toxicity burden from the contaminated soils can significantly affect yields, and energy balance and GHG emissions can be affected to a level that will not represent energy savings or emission reductions [3]. In fact, commonly, yields obtained in contaminated land are lower than in non-contaminated land [11, 12, 23, 25, 29]. This is because contaminated soils are also, frequently, deprived of organic matter and exhibiting losses in structure and holding capacity [3]. Lower yields reduce the amount of fossil energy saved/conserved, and the amount of GHG emissions saved, limiting the opportunities associated with the cultivation of energy crops in contaminated land [24, 30]. When the degree of land contamination is low and does not bring toxicity, or, when

the contaminants present low mobility, which will limit consequences on the plants, yields will not be affected and the resulting energy savings and GHG emissions savings will be secured [9].

3 Soil Function Restoration

The cultivation of energy crops in a contaminated soil presents several prospects, connected with the repair of soil properties (namely fertility and structure) and with the avoidance of conflicts on land use for food and feed. In fact, the presence of a vegetative cover and the assimilation of crops residues into soils will contribute to improve soil organic matter, will help to control soil erosion and will support boosting biodiversity and landscape diversity [3]. But, on the other hand, the lower yields obtained in contaminated land will bring the need to a higher area to produce the same amount of biomass feedstock for processing and use [23]. When considering postmining land, remediation may be scatter and not contiguous, which will bring heterogeneity to the landscape, enriching it [23].

Cultivation of energy crops in contaminated land will also help decreasing the soil degradation and contamination [11, 31]. The practice of using plants and their associated microbes, for soil decontamination, represent an opportunity, that is cost-effective, and solar-based and that will also contribute to amend the environmental risks associated with contamination [1, 2]. Energy crops present remediation features, namely high biomass, high tolerance to contamination, need of low inputs, and capacity to stabilize or reduce the degree of contamination in polluted soils. Short rotation coppices (e.g. willow and poplar), perennial crops (e.g. giant reed, miscanthus, switchgrass), annual crops (e.g. rapeseed, sunflower, Ethiopian mustard, hemp, kenaf) have demonstrated the ability to uptake metals or to biodegrade organic contaminants [3, 32, 33]. When time is an important factor to choose a technique to decontaminate soils, it should be taken into account that phytoremediation (phytoextraction, contaminants uptaken by the aerial fraction of crops – the harvested fraction, taken out from the field) is not an instant remediation technique. In fact, many years are needed to clean contaminated sites just by using phytoextraction (but phytoextraction can be applied with other treatment technologies, to help reducing the time needed for decontamination) [3, 31]. In the phytoextraction process, plants accumulate metals from soil in the biomass and its subsequent harvest, will contribute to the alleviation of the contamination of the soils [3]. Tolerance mechanisms presented by energy crops are usually linked with the accumulation of the contaminants in the belowground biomass and its reduced translocation to the harvested biomass [11]. This aspect represents also another opportunity, once the quality of the harvested biomass will present characteristics fitted to be exploited for bioenergy and biobased products.

4 Concluding Remarks

The phytoremediation of contaminated soils with energy crops represents an opportunity when compared to the derelict contaminated soils or to the traditional physical and chemical remediation techniques. From an environmental perspective, the restoration

of the contaminated soil will contribute to restore the land ecosystem services. From an economic point of view, but also from an environmental point of view, these energy crops can be used to replace fossil-based resources, either for bioenergy or for biobased products, which will provide additional revenue to owners. Moreover, economically, phytoremediation is also less costly than other traditional remediation techniques and presenting less harmful environmental effects. Advantages and constraints associated with the production of energy crops in contaminated soils are depicted in Fig. 1.

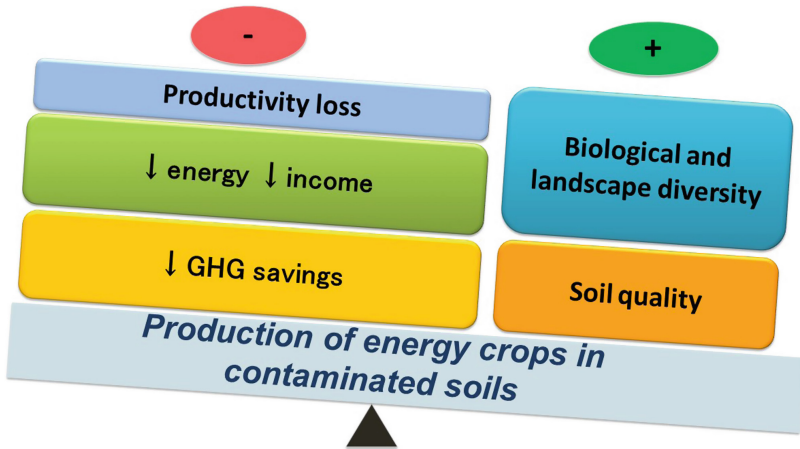


Fig. 1. Advantages and constraints associated with the production of energy crops in contaminated soils.

The revised literature shows that cultivating energy crops in contaminated soils have positive and less positive aspects compared with its production in non-contaminated soils. The productivity loss may reduce the energy and the greenhouse savings, but it may recover the quality of soil and waters and the landscape and biological diversity of those soils. The compilation of results presented in this work and future works that can show how combating climate change with phytoremediation is possible, should be clearly disseminated to several audiences and stakeholders (industry, cooperatives, farmers, etc.). It is important to indicate to farmers how they can add value to marginal and contaminated soils, through the production of industrial crops. The promotion of the achieved research and the developed guidelines will foster innovation and rural renaissance and will help to provide long-term benefits for the whole society. Moreover, dissemination actions will help to show that the introduction of industrial crops in contaminated soils will help to reduce competition for feed and food and land-use conflicts.

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References

1. Barbosa, B., Fernando, A.L.: Aided Phytostabilization of mine waste. In: Prasad, M.N.V., Favas, P.J.C., Maiti, S.K. (eds.) *Bio-Geotechnologies for Mine Site Rehabilitation*, Elsevier Inc., UK, 708, pp. 147–158 (2018). <https://doi.org/10.1016/B978-0-12-812986-9.00009-9>
2. Barbosa, B., Costa, J., Boléo, S., Duarte, M.P., Fernando, A.L.: Phytoremediation of inorganic compounds. In: Ribeiro, A.B., Mateus, E.P., Couto, N. (eds.) *Electrokinetics Across Disciplines and Continents*, pp. 373–399. Springer, Cham (2016). https://doi.org/10.1007/978-3-319-20179-5_19
3. Barbosa, B., Costa, J., Fernando, A.L.: Production of energy crops in heavy metals contaminated land: opportunities and risks. In: Li, R., Monti, A. (eds.) *Land Allocation for Biomass Crops*, pp. 83–102. Springer, Cham (2018). https://doi.org/10.1007/978-3-319-74536-7_5
4. Fernando, A.L., Boléo, S., Barbosa, B., Costa, J., Duarte, M.P., Monti, A.: Perennial grass production opportunities on marginal mediterranean land. *BioEnergy Res.* **8**, 1523–1537 (2015). <https://doi.org/10.1007/s12155-015-9692-0>
5. Oliveira, J.S., Duarte, M.P., Christian, D.G., Eppel-Hotz, A.: Fernando AL: environmental aspects of *Miscanthus* production. In: Jones, M.B., Walsh, M. (eds.), *Miscanthus for energy and fibre*. James & James (Science Publishers) Ltd., London, UK, 192, pp. 172–178 (2001)
6. Fernando, A.L., Rettenmaier, N., Soldatos, P., Panoutsou, C.: Sustainability of perennial crops production for bioenergy and bioproducts. In: Alexopoulou, E. (ed.) *Perennial Grasses for Bioenergy and Bioproducts*, Academic Press, Elsevier Inc., UK, 292, pp. 245–283 (2018). <https://doi.org/10.1016/B978-0-12-812900-5.00008-4>
7. Fernando, A.L., Godovikova, V., Oliveira, J.F.S.: *Miscanthus x giganteus*: contribution to a sustainable agriculture of a future/present – oriented biomaterial. *Mater. Sci. Forum, Adv. Mater. Forum* **II**(455–456), 437–441 (2004)
8. Fernando, A.L., Barbosa, B., Costa, J., Papazoglou, E.G.: Giant reed (*Arundo donax* L.): a multipurpose crop bridging phytoremediation with sustainable bio-economy, In: Prasad, M.N.V. (ed.) *Bioremediation and Bioeconomy*, Elsevier Inc., UK, 698, pp. 77–95 (2016). <https://doi.org/10.1016/B978-0-12-802830-8.00004-6>
9. Sidella, S., Barbosa, B., Costa, J., Cosentino, S.L., Fernando, A.L.: Screening of giant reed clones for phytoremediation of lead contaminated soils. In: Barth, S., Murphy-Bokern, D., Kalinina, O., Taylor, G., Jones, M. (eds.) *Perennial Biomass Crops for a Resource-Constrained World*, pp. 191–197. Springer, Cham (2016). https://doi.org/10.1007/978-3-319-44530-4_16
10. Barbosa, B., Costa, J., Fernando, A.L., Papazoglou, E.G.: Wastewater reuse for fiber crops cultivation as a strategy to mitigate desertification. *Ind. Crops Prod.* **68**, 17–23 (2015). <https://doi.org/10.1016/j.indcrop.2014.07.007>
11. Barbosa, B., et al.: Phytoremediation of heavy metal-contaminated soils using the perennial energy crops *Miscanthus* spp. and *Arundo donax* L. *BioEnergy Res.* **8**, 1500–1511 (2015). <https://doi.org/10.1007/s12155-015-9688-9>
12. Papazoglou, E.G., Fernando, A.L.: Preliminary studies on the growth, tolerance and phytoremediation ability of sugarbeet (*Beta vulgaris* L.) grown on heavy metal contaminated soil. *Indus. Crops Prod.* **107**, 463–471 (2017). <https://doi.org/10.1016/j.indcrop.2017.06.051>
13. Von Cossel, M., et al.: Prospects of bioenergy cropping systems for a more social-ecologically sound bioeconomy. *Agronomy* **9**(10), 605 (2019). <https://doi.org/10.3390/agronomy9100605>
14. Fernando, A.L., Duarte, M.P., Almeida, J., Boléo, S., Mendes, B.: Environmental impact assessment of energy crops cultivation in Europe. *Biofuels Bioprod. Biorefin.* **4**, 594–604 (2010). <https://doi.org/10.1002/bbb.249>
15. Dauber, J., et al.: Bioenergy from “surplus” land: environmental and socio-economic implications. *BioRisk* **7**, 5–50 (2012). <https://doi.org/10.3897/biorisk.7.3036>

16. Abreu, M., et al.: Gírio, F: Evaluation of the potential of biomass to energy in Portugal-conclusions from the CONVERTE project. *Energies* **13**(4), 937 (2020). <https://doi.org/10.3390/en13040937>
17. Von Cossel, M., et al.: Marginal agricultural land low-input systems for biomass production. *Energies* **12**(16), 3123 (2019). <https://doi.org/10.3390/en12163123>
18. Bouton, J.: Improvement of switchgrass as a bioenergy crop. In: Vermerris, W. (eds.) *Genetic Improvement of Bioenergy Crops*, pp. 309–345. Springer, New York (2008). https://doi.org/10.1007/978-0-387-70805-8_11
19. Barbosa, C.H., et al.: A new insight on cardoon: exploring new uses besides cheese making with a view to zero waste. *Foods* **9**(5), 564 (2020). <https://doi.org/10.3390/foods9050564>
20. Zanetti, F., Monti, A., Berti, M.T.: Challenges and opportunities for new industrial oilseed crops in EU-27: a review. *Ind. Crops Prod.* **50**, 580–595 (2013). <https://doi.org/10.1016/j.indcrop.2013.08.030>
21. Fernando, A.L., Costa, J., Barbosa, B., Monti, A., Rettenmaier, N.: Environmental impact assessment of perennial crops cultivation on marginal soils in the Mediterranean Region. *Biomass Bioenerg.* **111**, 174–186 (2018). <https://doi.org/10.1016/j.biombioe.2017.04.005>
22. Scordia, D., et al.: Towards identifying industrial crop types and associated agronomies to improve biomass production from marginal lands in Europe. *GCB Bioenergy*, pp. 1–25 (2022). <https://doi.org/10.1111/gcbb.12935>
23. Gomes, L.A., Costa, J., Santos, F., Fernando, A.L.: Environmental and socio-economic impact assessment of the switchgrass production in heavy metals contaminated soils. In: Machado, J., Soares, F., Trojanowska, J., Ottaviano, E. (eds.) *Innovations in Mechanical Engineering. icieng 2021. Lecture Notes in Mechanical Engineering*. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-79165-0_38
24. Boléo, S., Fernando, A.L., Duarte, M.P., Mendes, B.: Environmental and socio-economic impact assessment of the Miscanthus production in Zn contaminated soils. In: Castro, F., Vilarinho, C., Carvalho, J., Castro, A., Araújo, J., Pedro, A. (eds.) *Book of proceedings 2nd International Conference: Wastes: solutions, treatments and opportunities*, 11–13 September 2013, Braga, Portugal, CVR, Centro de Valorização de Resíduos, pp. 657–662 (2013)
25. Schmidt, T., Fernando, A.L., Monti, A., Rettenmaier, N.: Life cycle assessment of bioenergy and bio-based products from perennial grasses cultivated on marginal land in the mediterranean region. *BioEnergy Res.* **8**, 1548–1561 (2015). <https://doi.org/10.1007/s12155-015-9691-1>
26. Fernando, A.L., Duarte, M.P., Vatsanidou, A., Alexopoulou, E.: Environmental aspects of fiber crops cultivation and use. *Ind. Crops Prod.* **68**, 105–115 (2015). <https://doi.org/10.1016/j.indcrop.2014.10.003>
27. Ardente, F., Beccali, M., Cellura, M., Mistretta, M.: Building energy performance: A LCA case study of kenaf-fibers insulation bord. *Energ. Buildings* **40**, 1–10 (2008)
28. Cherubini, F., Bird, N.D., Cowie, A., Jungmeier, G., Schlamadinger, B., Woess-Gallasch, S.: Energy- and greenhouse gas-based LCA of biofuel and bioenergy systems: key issues, ranges and recommendations. *Resour. Conserv. Recy.* **53**, 434–447 (2009)
29. Boléo, S., Fernando, A.L., Barbosa, B., Costa, J., Duarte, M.P., Mendes, B.: Remediation of soils contaminated with Zinc by Miscanthus. In: Vilarinho, C., Castro, F., Russo, M. (eds.) *WASTES 2015–Solutions, Treatments and Opportunities: Selected papers from the 3rd Edition of the International Conference on Wastes: Solution, Treatments and Opportunities*, Viana do Castelo, Portugal, September 2015, pp. 37–42. CRC Press, Taylor & Francis Group (2015)

30. Fernando, A.L., Barbosa, B., Costa, J., Alexopoulou, E.: Perennial grass production opportunities and constraints on marginal soils. In: Faaij, A.P.C., Baxter, D., Grassi, A., Helm, P. (eds.) *Proceedings of the 24rd European Biomass Conference and Exhibition, Setting the course for a Biobased Economy*, Amsterdam, The Netherlands, June 2016, ETA-Florence Renewable Energies, pp. 133 – 137 (2016)
31. Pidlisnyuk, V., Stefanovska, T., Lewis, E.E., Erickson, L.E., Davis, L.C.: Miscanthus as a productive biofuel crop for phytoremediation. *Crit. Rev. Plant. Sci.* **33**, 1–19 (2014)
32. Cumbane, B., et al.: Is the production of Kenaf in heavy metal contaminated soils a sustainable option?. In: *Wastes: Solutions, Treatments and Opportunities III*, pp. 512–517. CRC Press (2019)
33. Arora, K., Sharma, S., Monti, A.: Bio-remediation of Pb and Cd polluted soils by switchgrass: a case study in India. *Int. J. Phytoremediation* **18**, 704–709 (2016)



Obtaining New Alkali-Activated Binders from Waste of Different Sources

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Abstract. In last decades, more eco-friendly cements have been studied to replace the conventional Portland cement. The most prominent binders have been alkali-activated materials or geopolymers. These materials are obtaining good results in terms of mechanical resistance, durability and thermal conductivity. But its behaviour depends on the origin of the raw material and the activator used.

A comparative study has been developed using two different slags: copper slag (CUS) and ferrosilicon slag (FES); and biomass bottom ash (BBA) as precursors. Raw materials were characterized using Fourier transform infrared spectroscopy (ATR-FTIR) and X-Ray Diffraction (XRD). The CUS and FES waste were used individually and mixed with BBA. They were activated with a solution of 65% wt K_2SiO_3 and 35% wt KOH (8M). The curing stage was carried out in a climatic chamber at 20 °C and 90% RH for 1, 7, 28 and 90 days. Mechanical and thermal tests were performed on specimens, and compared with OPC paste specimens. Besides alkali-activated cement manufactured were analyzed using ATR-FTIR.

Results show that depending on the origin of the slag, some properties can be improved by adding biomass ashes. In particular, alkali-activated cements manufactured mixing FES and BBA, mechanical properties are improved. However, in the case of CUS, they obtained better results when they were used individually.

Keywords: Alkali activated cements · Bottom biomass ash · Ferrosilicon slag · Copper slag

1 Introduction

New materials to replace ordinary Portland cement have been appearing, although materials with best results are alkali activated materials or geopolymers [1]. They have developed good mechanical strength, durability properties and low thermal conductivity [2, 3]. These materials are formed by a precursor and an alkaline activator. Properties developed depend on raw materials selected [1]. Materials from different sources, natural and residues, have been used, but researchers are more interested in using waste to reduce landfills and CO₂ emissions [3].

One of the most investigated raw materials have been slags [4–6]. Slags are a by-product from metallurgical industry, one of the largest producers of waste, which it has seen its production increase in recent years, in the case of copper [7]. The world copper production is about 20.8 million tons [8]. In Spain, 600,000 ton/year of CUS are produced [9]. Copper slag (CUS) is a by-product generated in the copper extraction and treatment processes such as blowing, refining and smelting. The latter process in particular produces the largest amount of copper slag [10]. It is estimated that in the production of 1 tonne of copper, between 2 and 3 tonnes of copper slag are produced [11–13]. One of the reasons for not being able to reuse copper slag is that one of its major components, fayalite, produces silica gel during its dissolution process [14]. Ferrosilicon slag (FES) is a by-product material of silicon and ferrosilicon industries after smelting, cooling and reducing procedures high-purity quartz using coal in an electric arc furnace. As a result, irregular shape of particles of various sizes rich in silica minerals is obtained [15]. The production of ferrosilicon slag is estimated between 0.9 and 2.2 tonnes of slags for each ton of material produced [12]. In Spain 200,000 ton/year of FES are generated [12]. Ferrosilicon slag has a high amount of free silicon, so given its low cost, it is used in steel-making and Portland cement industries [6].

Besides, it is betting on energy of biomass origin, which represents 70% of renewable energy produced and 6% of the total primary energy [16]. The cement consumption in Spain is 15 million ton/year [17]. The use of slag generated in the copper and ferroalloy industry, together with waste generated in biomass energy production in the production of alkaline activated cements, could considerably reduce cement consumption, especially in areas close to the production of these wastes. The production of these new binders would not only save natural raw materials but also energy consumption. Slags of different origins have been used as a source of aluminosilicates both individually [18] and mixed with other wastes, mainly fly ash [19], to a lesser extent bottom ash [20]. In this study have been used CUS and FES, and they were mixed with biomass bottom ash (BBA). This ash is generated after combustion of pine, olive pruning and olive pomace in electric power plant.

The target of this study is to take advantage of the metallurgical slag, together with the waste generated from production of biomass energy, reducing the cement consumption considerably and landfill. Different pastes were synthesized using 100% wt of raw material and mix 50% wt of each precursor. Portland cement paste was manufactured as a control paste. Binder manufactured were characterized by ATR-FTIR, mechanical strength and thermal conductivity.

2 Materials and Methods

2.1 Raw Materials

Biomass waste and by-product of metallurgical industry were used as raw materials in this study. Copper slag (CUS) was supplied by Atlantic Copper, sited in Huelva (Spain). These slags are generated in the refining process of copper [21]. Ferrosilicon slag (FES) was provided by Ferroatlántica, located in A Coruña (Spain). They are produced in the process of smelting ferrosilicon [15]. Biomass bottom ash come from an electric power

plant, Aldebarán Energía del Guadalquivir in Andújar (Jaén, Spain). All precursors were ground below 100 μm .

Chemical composition of raw materials is shown in Table 1, and it was obtained by X-Ray fluorescence (XRF) using a Philips Magix Pro model PW-2440. FES is formed mainly for SiO_2 and CaO , and significant content of Al_2O_3 and MnO . In the case of CUS, predominant component is Fe_2O_3 , with high value of SiO_2 . The main component in BBA is SiO_2 , with important quantities of Al_2O_3 and CaO .

Table 1. Chemical composition of precursors.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	SO_3	LOI
FES	38.92	13.53	0.81	26.22	4.74	10.31	0.39	1.28	2.20	0.00
CUS	27.65	2.04	62.18	1.25	0.38	0.03	0.63	0.56	0.90	0.00
BBA	46.10	12.04	4.78	19.65	3.71	0.09	0.78	4.59	0.41	5.58

Crystalline mineralogical phases of raw materials were identified by X-Ray diffraction (XRD) by Empyrean equipment with a PIXcel-3D detector from PANalytical using Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) at a voltage of 40 kV and an amperage of 40 mA. High amorphous structure was found in the diffractogram of FES and CUS. FES present manganese oxide (Mn_3O_4), quartz (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and akermanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$) as crystalline mineralogical phases. In the case of CUS, fayalite ($(\text{Fe}^{2+})_2\text{SiO}_4$) and magnetite (Fe_3O_4) are the phases identified. In BBA were identified peaks of quartz, calcite (CaCO_3), lime (CaO) and aluminosilicates.

2.2 Manufacture of Pastes

Precursors were used in different proportion following the structure: 100% wt of precursor, and 50% wt ashes with 50% wt slags (Table 2). Raw materials were put into a mixer and they were mixed for 90 s. After, the activator solution was poured. In this study, the activator used was a mix of 65% wt KOH (8M) and 35% wt K_2SiO_3 , and the liquid/solid (l/s) ratio is showed in Table 2. The activator and precursors were mixed for 90 s. Then material on the wall of mixer were removed with a scraper. Fresh pastes were poured into prismatic steel moulds ($60 \times 10 \times 10 \text{ mm}$) for mechanical properties and cylindrical plastic moulds ($\phi 55 \text{ mm}$) for thermal properties, and they were placed in a climatic chamber at 20 $^\circ\text{C}$ and 90% RH. After 24 h, pastes were demoulded and they were stored in climatic chamber at same conditions. Mechanical and physical test were developed at 1, 7, 28 and 90 days of curing and thermal conductivity at 28 days. As well alkali-activated cements were characterized by ATR-FTIR at 7 days of curing.

3 Results and Discussion

3.1 Mechanical Strength

Mechanical strength results are shown in Fig. 2 (flexural strength) and Fig. 3 (compressive strength) over time of curing. The best value for flexural strength in alternative pastes

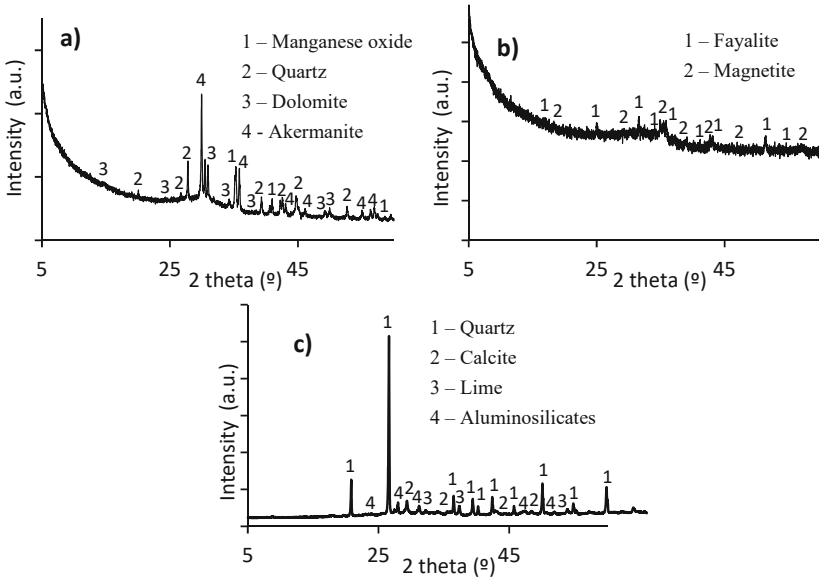


Fig. 1. Diffractograms of raw materials: a) FES, b) CUS and c) BBA.

Table 2. Alkali-activated cements manufactured and codes.

Code	% wt ash	% wt slag	Slag used	l/s ratio
100FES	0	100	FES	0.60
50BBA-50FES	50	50	FES	0.60
100CUS	0	100	CUS	0.35
50BBA-50CUS	50	50	CUS	0.35
100BBA	100	0	–	0.60
OPC	100% OPC		–	0.50

was obtained by 100CUS after 90 days of curing, around 9 MPa This value is higher than those obtained by other authors using CUS [22] and it is not far from the flexural strength obtained for control paste 100OPC (9.4 MPa). Near this value, around 8 MPa was achieved when CUS were mixed with BBA. Flexural strength value for 100FES was very poor, although resistance improved when they were mixed with BBA. They even exceeded the flexural value of 100BBA. The different trend registered for 100 FES could be due to superficial fissures that they were identified with the naked eye. These cracks weakened samples, making it less resistant to flexural strength.

Compressive strength results shown values with the same trend than flexural strength, except using 100% wt of FES. In this case, the compressive strength was high without to mix them with BBA. The compressive strength increases with curing time. The highest value after 90 days of curing was achieved for 100 CUS (60 MPa). Followed by specimens

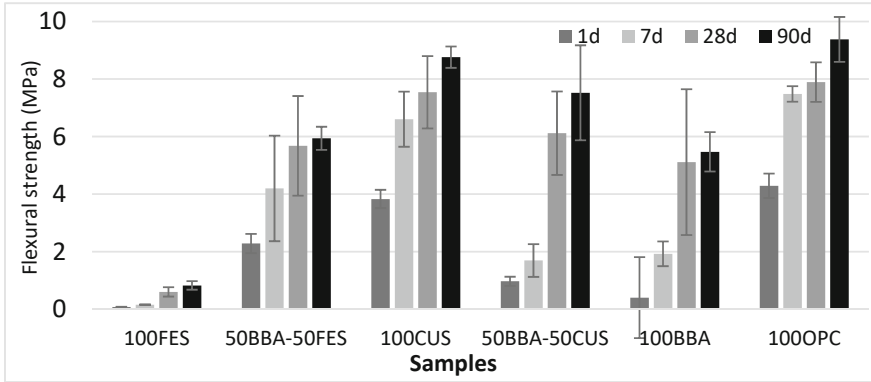


Fig. 2. Flexural strength over time for pastes manufactured.

50BBA-50CUS (45 MPa) and 100FES (40 MPa). Mixing FES and BBA were also obtained high values (30 MPa). Values obtained for 100FES were better than other authors. For instance, Ahmed et al. registered between 4–6 MPa using different activators with 100% wt of FES [6]. 100CUS, 50BBA-50CUS and 100FES samples exceeded the OPC resistance (34 MPa) at 90 days of curing, even 50BBA-50FES stayed close to this value. 100OPC results are lower than other studies [23, 24] due to a high l/s ratio was used [24]. Even so, 100CUS specimens reached greater compressive strength than that obtained by these authors for Portland cement specimens. The difference in the mechanical properties could be due to the difference in densification of the specimens depending on the slag used, or the mixture slag-ash, as well as the amount and type of geopolymeric gel formed.

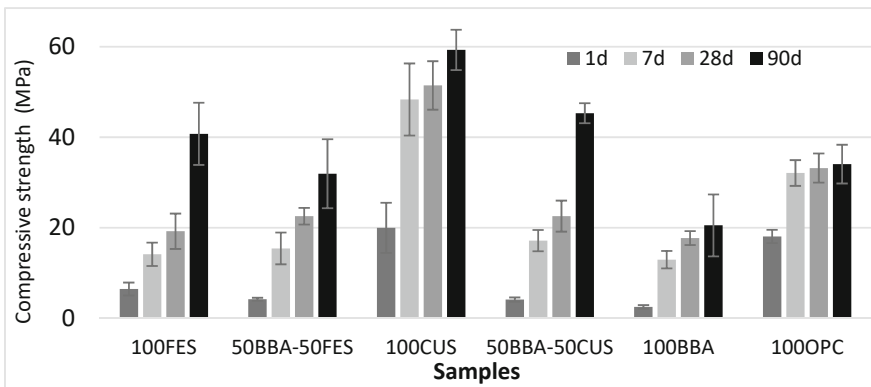


Fig. 3. Compressive strength over time for pastes manufactured.

3.2 FTIR

ATR-FTIR results are represented in the Fig. 4 for specimens at 7 days of curing. The characteristic bands of alkali activated materials were identified between $945\text{--}962\text{ cm}^{-1}$. These bands belong to *Si-O-Si* and *Si-O-Al* bonds [25, 26] indicating that the process of geopolymerization or alkaline activation has taken place. O-H bonds were found centred at 3200 cm^{-1} and 1645 cm^{-1} , they are attributed to water molecules, they are necessary to geopolymerization process [6]. At 1412 cm^{-1} was found a band correspond to C-O bonds, presence of $(\text{CO}_3)^{-2}$ [5], it not found for 100CUS. A band centred at 875 cm^{-1} was identified attributed to C-O-C or Si-O-Fe bonds [20].

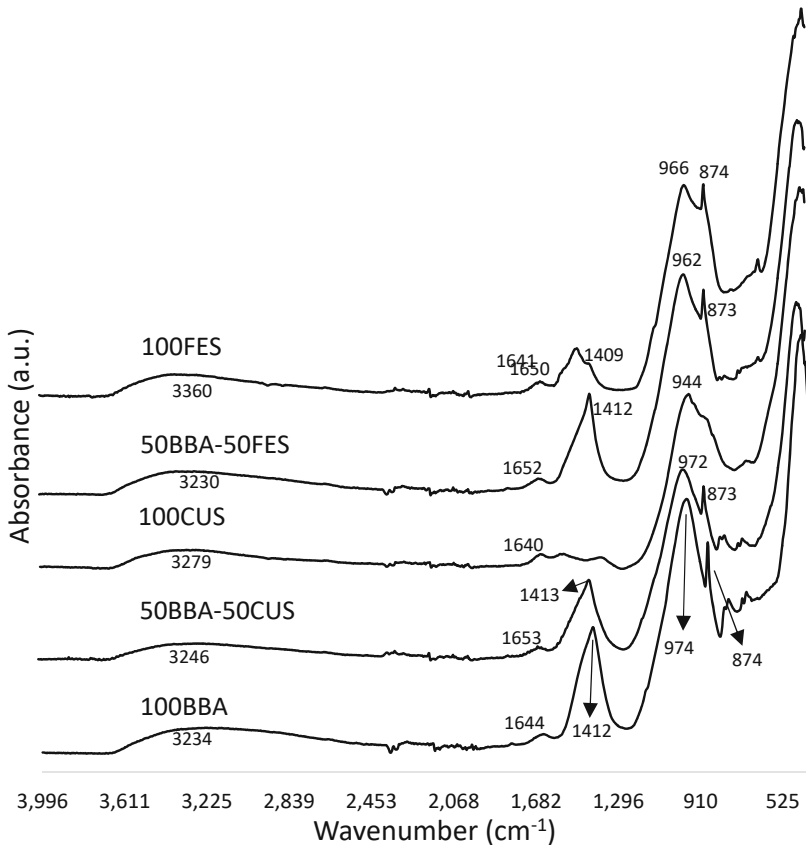


Fig. 4. ATR-FTIR spectrograms of alkali activated cements at 7 days of curing.

3.3 Thermal Conductivity

Values of thermal conductivity at 28 days of curing are presented in Fig. 5. All specimens obtained better results than results obtained using conventional Portland cement

(0.44 W/mK), and compared with data from other authors [23, 27, 28]. However, the best value was achieved for 100CUS (0.25 W/mK). Nevertheless, the thermal conductivity of the remaining specimens was between 0.30–0.31 W/mK, indicating the insulating capacity of these alkali activated cements.

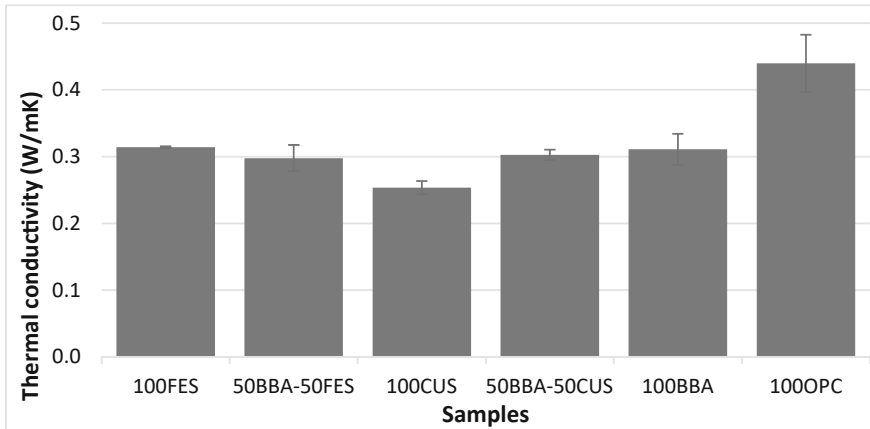


Fig. 5. Thermal conductivity of alkali activated cements at 28 days of curing.

4 Conclusions

A comparison of behaviour of alkali activated materials from different sources was developed. Best materials after 90 days of curing was using 100% wt of CUS: flexural strength was 9 MPa, and compressive strength of 60 MPa, exceeding values reached by OPC. 100 FES specimens presented problems of cracks, for this reason flexural strength result were very low.

The effect to replace slags by BBA was also analysed:

- BBA + FES: Final flexural strength improved; but compression strength decreased.
- BBA + CUS: Mechanical properties got worse. Although results were satisfactory.

ATR-FTIR results confirmed the presence of geopolymeric gel formation along the curing time for all specimens (Si-O-T bonds). Besides values of thermal conductivity obtained were very low and better than OPC, revealing the insulating capacity of these materials. From the results, these wastes can be used as raw material for the manufacture of alkali activated cements as alternative to ordinary Portland cement.

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References

1. Provis, J.L.: Alkali-activated materials. *Cem. Concr. Res.* **114**, 40–48 (2018)
2. Ge, X., Hu, X., Shi, C.: The effect of different types of class F fly ashes on the mechanical properties of geopolymers cured at ambient environment. *Cement Concr. Compos.* **130**, 104528 (2022)
3. Hui-Teng, N., et al.: Comparison of thermal performance between fly ash geopolymer and fly ash-ladle furnace slag geopolymer. *J. Non-Crystalline Solids* **585**, 121527 (2022)
4. Chaitanya, B.K., Kumar, I.S.: Effect of waste copper slag as a substitute in cement and concrete-a review. In: *IOP Conference Series: Earth and Environmental Science*, vol. 982, no. 1, p. 012029. IOP Publishing (2022)
5. Luo, Z., Hao, Y., Mu, Y., Tang, C., Liu, X.: Solidification/stabilization of red mud with natural radionuclides in granular blast furnace slag based geopolymers. *Constr. Build. Mater.* **316**, 125916 (2022)
6. Ahmed, M.M., et al.: Fabrication of thermal insulation geopolymer bricks using ferrosilicon slag and alumina waste. *Case Stud. Constr. Mater.* **15**, e00737 (2021)
7. Phiri, T.C., Singh, P., Nikoloski, A.N.: The potential for copper slag waste as a resource for a circular economy: a review–Part I. *Miner. Eng.* **180**, (2022)
8. World Mining Data, data section. https://www.world-mining-data.info/?World_Mining_Data_Data_Section. Accessed 15 Jun 2022
9. Alonso-Álvarez, E., García-Vila, P.: Declaración Ambiental Año 2021. Grupo de Medio Ambiente de Atlantic Copper, S.L.U., Huelva (2022)
10. Zuo, Z., et al.: Advances in recovery of valuable metals and waste heat from copper slag. *Fuel Process. Technol.* **235**, 107361 (2022)
11. Zhang, H., Li, B., Wei, Y., Wang, H., Yang, Y.: Effect of MgO on physicochemical property and phase transformation in copper slag. *J. Mater. Res. Technol.* **18**, 4604–4616 (2022)
12. Jiménez-Guerra, C., Díaz-Rodríguez, A., Fernández-Arauzo, E.: Análisis de la aplicación del concepto de fin de condición de residuo de las escorias de fundición de horno de arco eléctrico -acero al carbono, cobre y silicomanganeso- para su uso como árido (en aplicaciones ligadas y no ligadas) y otros usos: como materia prima en la fabricación de productos de construcción (cemento y clínker) y como material abrasivo. Ministerio para la transformación ecológica y el reto demográfico, Madrid (2021)
13. Han, B., et al.: Development of copper recovery process from flotation tailings by a combined method of high–pressure leaching–solvent extraction. *J. Hazard. Mater.* **352**, 192–203 (2018)
14. Wang, Q., Ma, H., Liu, M., Guo, R., Liu, G.: A new method of full resource utilization of copper slag. *Hydrometallurgy* **212**, 105899 (2022)
15. Kim, H., Ann, K.Y.: Applicability of ferrosilicon slag for a cementitious binder in concrete mix. *Constr. Build. Mater.* **271**, 121873 (2021)
16. De Gregorio, M.: Biomasa en España. Generación de valor añadido y análisis prospectivo. *Presupuesto y Gasto Publico* **97**, 41–57 (2019)
17. Oficemen, press release. <https://www.oficemen.com/el-consumo-de-cemento-crece-un-11-en-2021/>. Accessed 15 Jun 2022

18. Li, C., Sun, H., Li, L.: A review: The comparison between alkali-activated slag (Si + Ca) and metakaolin (Si + Al) cements. *Cem. Concr. Res.* **40**(9), 1341–1349 (2010)
19. Zhang, P., Gao, Z., Wang, J., Guo, J., Hu, S., Ling, Y.: Properties of fresh and hardened fly ash/slag based geopolymer concrete: a review. *J. Clean. Prod.* **270**, (2020)
20. Gómez-Casero, M.A., Pérez-Villarejo, L., Castro, E., Eliche-Quesada, D.: Effect of steel slag and curing temperature on the improvement in technological properties of biomass bottom ash based alkali-activated materials. *Constr. Build. Mater.* **302**, 124205 (2021)
21. Singh, J., Singh, S.P.: Synthesis of alkali-activated binder at ambient temperature using copper slag as precursor. *Mater. Lett.* **262**, 127169 (2020)
22. Singh, N., Gupta, A., Haque, M.M.: A review on the influence of copper slag as a natural fine aggregate replacement on the mechanical properties of concrete. In: *Materials Today: Proceedings* (2022)
23. Du, Y., Yang, W., Ge, Y., Wang, S., Liu, P.: Thermal conductivity of cement paste containing waste glass powder, metakaolin and limestone filler as supplementary cementitious material. *J. Clean. Prod.* **287**, 125018 (2021)
24. Park, S., Moges, K.A., Wu, S., Pyo, S.: Characteristics of hybrid alkaline cement composites with high cement content: flash set and high compressive strength. *J. Mater. Res. Technol.* **17**, 1582–1597 (2022)
25. Kljajević, L.M., et al.: Structural and chemical properties of thermally treated geopolymer samples. *Ceram. Int.* **43**(9), 6700–6708 (2017)
26. Aziz, A., et al.: Effect of blast-furnace slag on physicochemical properties of pozzolan-based geopolymers. *Mater. Chem. Phys.* **258**, 123880 (2021)
27. Liu, C., Qian, R., Liu, Z., Liu, G., Zhang, Y.: Multi-scale modelling of thermal conductivity of phase change material/recycled cement paste incorporated cement-based composite material. *Mater. Des.* **191**, 108646 (2020)
28. Park, H.M., et al.: Influence of Portland cement and alkali-activated slag binder on the thermoelectric properties of the p-type composites with MWCNT. *Constr. Build. Mater.* **292**, 123393 (2021)

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