Energy Footprint of Biorefinery Schemes

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Abstract Biorefineries are evolving systems that have great potential to replace traditional oil-based alternatives. The concept of biorefinery addresses a comprehensive approach to the manufacture of bio-products and bioenergy. The intrinsic objective of a biorefinery is not to exclusively produce a single value-added bio-product such as cellulose, bioethanol, furfural, hydroxymethyl furfural, etc. The overall aim is to achieve a multi-product system with the flexibility to handle and transform different feedstocks. Different configurations evaluate the treatment of food and feed crops (first generation biorefinery), lignocellulosic biomass (second generation biorefinery) and algae (third generation biorefinery). The aim of this study is to assess the state of the art in terms of Life Cycle Assessments of biorefineries and to discuss the impact of energy consumption on global environmental outcomes. Although there is a widespread belief that biorefineries are systems with lower environmental impacts than oil-based refineries, they are energy-intensive systems with high electricity, steam and heat requirements. Therefore, a common hotspot for biorefining processes is energy consumption. The present study highlights the discussion of concepts such as the energy consumption profile of biorefineries with the aim of determining the sections of the biorefinery that could potentially contribute with higher burdens to the energy footprint of the plant. On the other hand, the evaluation of different biorefinery schemes with different functions depending on the products, raises the need to introduce concepts such as eco-efficiency to allow the comparability of the energy footprint of different scenarios. In the current framework, in which most biorefineries are pilot plants that aim to demonstrate the technical feasibility of the process under development, it is also relevant to consider aspects of energy integration and optimization. Under this

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S. S. Muthu (ed.), *Energy Footprints of the Bio-refinery, Hotel, and Building Sectors*,
Environmental Footprints and Eco-design of Products and Processes,
https://doi.org/10.1007/978-981-13-2466-6_1

perspective, future research has room for improvement in terms of energy use. The underlying concept is to analyze the current framework for biorefinery industries and establish benchmarks to address future research and implementation of eco-friendly alternatives. The present study suggests that industrial implementation of biorefineries in real scale systems should come with far more optimization for the achievement of sustainability. Specifically, the production of energy to fulfill the biorefinery's demand can be highlighted as one of the processes that represent clear environmental burdens. Also, pre-treatment of lignocellulosic feedstock, due to the recalcitrant nature of the biomass, can be pinpointed as an area of improvement towards the minimization of the biorefinery's energy footprint.

Keywords Biorefinery · Eco-efficiency · Energy footprint · Life cycle assessment Lignocellulosic biomass · Second generation biorefinery · Sustainability

AC	Acidification
AD	Abiotic depletion
AETP	Aquatic ecotoxicity potential
ALO	Agricultural land occupation
AP	Acidification potential
CAPs	Selected criteria air pollutants
CC	Climate change
CED	Cumulative energy demand
CED-F	Cumulative energy demand, fossil
CED-T	Cumulative energy demand, total
CHP	Combined heat and power
EC	Ecotoxicity
EIP	Exergy improvement potential
EP	Eutrophication potential
EROEI	Energy return on energy invested
EROI	Energy return on investment
EU	Eutrophication
FD	Fossil depletion
FDCA	Furandicarboxylic acid
FE	Freshwater eutrophication
FEC	Fossil energy consumption
FER	Fossil energy ratio
FET	Freshwater ecotoxicity
FEU	Fossil energy use
FU	Functional unit
GHG	Greenhouse gas
GVA	Gross value added
GWP	Global warming potential
HHC	Human health cancer
HHNC	Human health non-cancer
HMF	Hydroxymethyl furfural

HT	Human toxicity
HT-C	Human toxicity, cancer
HT-NC	Human toxicity, non-cancer
HTP	Human toxicity potential
ILUC	Indirect land use change
IR	Ionizing radiation
LCA	Life cycle assessment
LCB	Lignocellulosic biorefinery
LHV	Low heating value
MD	Minerals depletion
ME	Marine eutrophication
MEC	Marine ecotoxicity
ME-Plim	Phosphorous-limited marine eutrophication
MET	Marine ecotoxicity
MOO	Multi objective optimization
NEG	Net energy gain
NER	Net energy ratio
NEV	Net energy value
NLT	Natural land transformation
NRE	Non-renewable energy
NREU	Non-renewable energy used
OD	Ozone depletion
ODP	Ozone layer depletion potential
PA	Polyamide
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoate
PLA	Polylactic acid
PM	Particulate matter
PMF	Particulate matter formation
PO	Photochemical oxidation
POCP	Photochemical oxidant potential
POF	Photochemical oxidant formation
POP	Photochemical oxidation potential
PS	Polystyrene
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
REU	Renewable energy used
SED	Specific energy demand
SMG	Smog formation
SS	Subsystem
TA	Terrestrial acidification
TCF	Total chlorine-free

TET	Terrestrial ecotoxicity
TETP	Terrestrial ecotoxicity potential
TOPO	Trioctylphosphine oxide
TRL	Technology readiness level
ULO	Urban land occupation
WC	Water consumption
WD	Water depletion
WS	Water scarcity

1 Introduction. The Biorefinery Concept

The foreseeable depletion of fossil fuels demands a change in the present productive and economic structure. The development of an alternative scheme has been proposed with a view to reducing finite availability fossil resources in favor of renewable biological resources. The European Commission has set ambitious targets for reducing greenhouse gas emissions by 20% and, in parallel, increasing the use of renewable energy and energy efficiency (European Commission 2018). Within this framework, the concept of biorefinery emerges as an alternative to oil-based refineries, which requires the development of new processes through research, pilot plants and exploitation on an industrial scale (Elvnert 2009). An increasing proportion of chemicals, plastics, fuels and electricity are expected to come from biomass in the forthcoming decades. Because of its broad scope and the different drivers behind it, the sustainability of bioeconomy is expected to address important challenges in relation to social, economic and environmental aspects.

Moving from philosophy to practice, biorefineries integrate processes that convert a single biomass source into a range of biochemical materials (chemicals, materials), biofuels and bioenergy (power, heat). The core idea of a biorefinery is analogous to that of oil refineries, being both multi-product systems. Biorefineries however should engage in considering sustainability criteria, in order to compensate for low efficiencies in biomass conversion processes (King 2010).

The history of the existing corn wet-milling industry can be seen as an example of how the biorefinery of the future will evolve. Initially, the corn wet milling industry produced starch as the main product. As technology developed and the need for higher value products fostered the growth of the industry, the product portfolio expanded from starch derivatives such as glucose and maltose syrups to high fructose corn syrup. Subsequently, fermentation products derived from starch and glucose such as citric acid, gluconic acid, lactic acid, lysine, threonine and ethanol were included in the production scheme. Many other by-products such as corn gluten, corn oil, corn fiber and animal feed are currently being produced. Refineries based on lignocellulosic biomass are undergoing a similar evolution in which the product portfolio is expanding from basic wood fractions (lignin, hemicellulose and cellulose) to the production of higher value added bioproducts (mainly ethanol, but also chemicals such as furfural, hydroxymethyl furfural or furandicarboxylic acid).

In this context, there are increasing examples of biotechnology-based chemicals and materials: ethylene and isobutanol, polymers such as polylactic acid (PLA), polyethylene (PE), polyhydroxyalkanoate (PHA), enzymes, flax and hemp-reinforced composites, all of which are produced from biological feedstocks. The field of biorefinery opens up opportunities to study the environmental sustainability of processes and the relevance of environmental impacts with respect to petrochemical alternatives. Without losing the perspective of technological viability, it is necessary to address the environmental assessment of these developing processes. With this objective in mind, the consideration of the energy consumption profiles of biorefineries will make it possible to determine whether biorefineries will play a significant role in achieving the Horizon 2020 climate and energy goals. Figure 1 presents a general overview of the biorefinery approach, considering multiple products, different feedstocks and a wide range of technologies (Kamm and Kamm 2004).

A simplified comparative analysis of the basic principles of both oil and biomass refineries makes it possible to identify as a differentiating element the previous stages for the conditioning of raw materials. The petrochemical industry works on the principle of generating simple and well-defined pure products from hydrocarbons in refineries. This principle can be transferred and extrapolated to biorefineries (Fig. 2).

The aim of this chapter is to establish a basic roadmap for biorefineries under the perspective of the energy footprint. First, a review of bibliographic studies was carried out to address the state of the art in the environmental assessment of biorefineries and to analyze how the energy aspect has been described. On the other hand, an overview of biorefinery facilities in Europe has been approached with the aim of analyzing, at first hand, the state of the art on built or planned facilities. Secondly, an industrial case study has been assessed according to the life-cycle assessment approach focusing on the identification of critical process hot spots originated in the energy needs of the installation. Some concepts related to the energy footprint such as net energy gain, eco-efficiency and energy integration have been revised to provide a comprehensive view of the energy sustainability of biorefineries.

1.1 Biorefinery Configurations Attending to Feedstock

The value chain of a biorefinery is built around two relevant entities: the type of feedstock used and the separation process of the different products. Within the biorefinery, different types of biomass can be used for industrial purposes: energy crops and forestry biomass, agricultural food and feed, crop residues, aquatic plants, animal wastes and other waste materials including those from food and feed

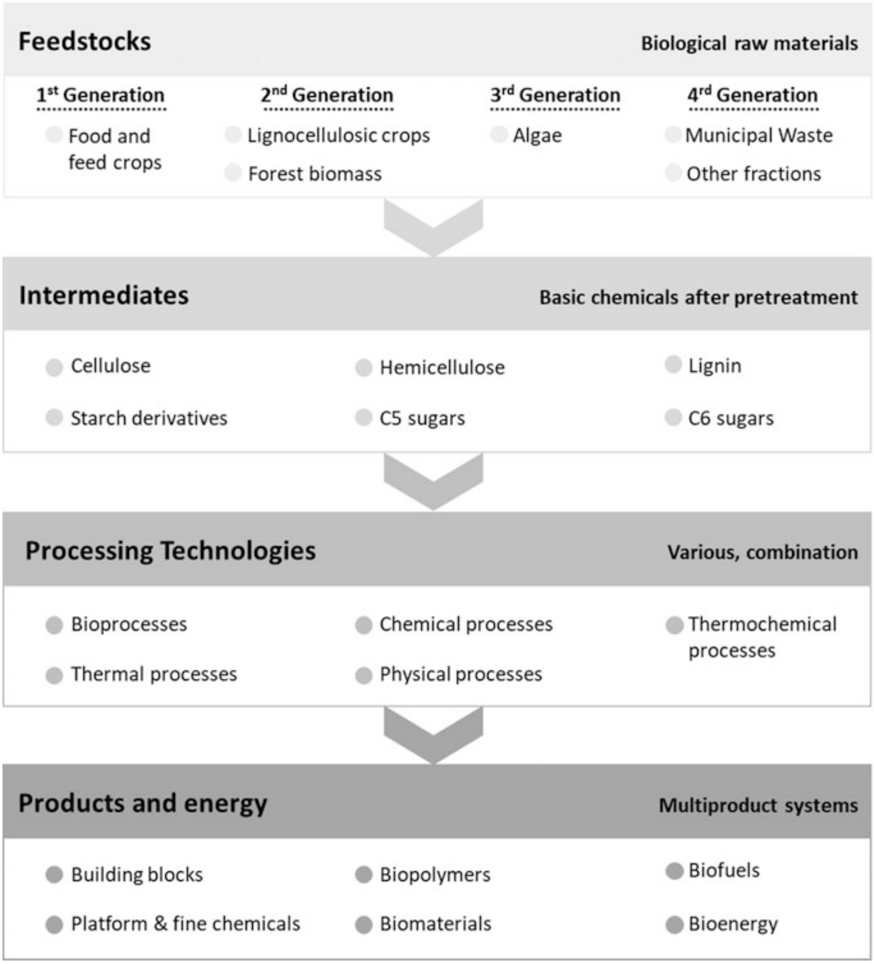

Fig. 1 Principles of a biorefinery Adapted from Kamm and Kamm (2004)

processing (Eaglesham et al. 2000). Taking the supply chain of polylactic (PLA) as an example, sugar-based biomass (e.g. sugar cane, sugar beet, etc.) is used as a substrate to obtain lactic acid or lactides. These lactides eventually form the basis of PLA, which can be sold as such and/or used to produce other consumer end products.

Some authors suggest the existence of four different biorefinery configurations that have been defined according to the type of feedstock they intend to exploit. Obviously, the biomass to be processed affects the viability of the technologies to be used in each case. Generally speaking, the exploitation and processing of bio-based feedstocks will be closely linked to the technology needs and the energy consumption of processes. In terms of potential profitability, it is important to

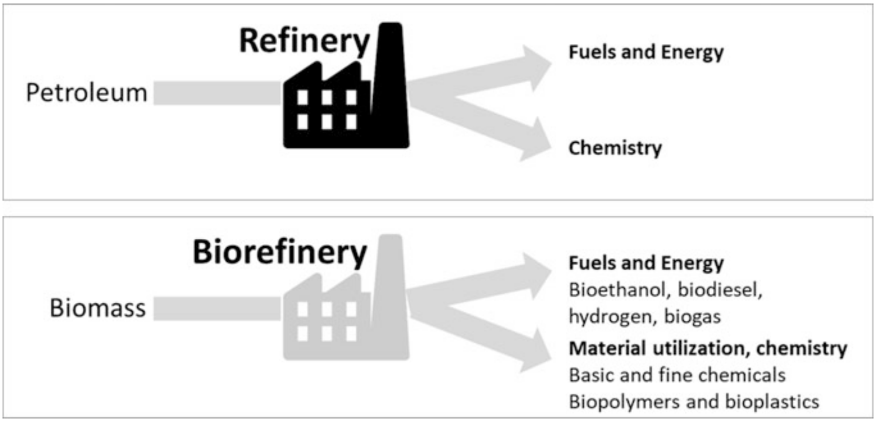

Fig. 2 Basic principles of traditional refinery and biorefinery Adapted from Kamm et al. (2008)

assess the strengths, weaknesses, challenges and opportunities that can be effectively applied to improve the prospects for a sustainable biotechnology-based economy.

Biomass production systems, supply chains and end-uses differ widely, according to different feedstocks, and so do their environmental and socioeconomic impacts (e.g. carbon stocks, water, soil, air, biodiversity, land use change and food security). The direction (positive or negative) and magnitude of these impacts mainly depend on the type of feedstock, biophysical and socio-economic conditions of the production site, production technologies, supply chain and end-use.

1.1.1 First Generation Biorefineries

The use of agricultural resources in industry was first proposed in the 18th century with the development of technologies for corn refining. This achievement marked the first step towards the evolution of the biorefinery approach. Until the conquest of the lead position by crude oil as the primary fuel in the industrialization process of the 19th and 20th centuries, extensive exploitation of biomass was mainly linked to the use of agricultural resources (Kamm et al. 2016).

Today, first-generation biorefineries are facilities that exploit edible crops such as grains, sugar, starch or oilseeds. Some of the most common food crops processed in biorefineries are maize, wheat, triticale, sorghum, rice, sugar cane, sugar beet, cassava, soybean, oil palm and rapeseed (Cassman and Liska 2007). In Europe and North America, most bioethanol is produced from maize and wheat (Vohra et al. 2014). However, it is recognized that the production of first-generation sugars implies the need for large quantities of feedstocks available at an uncompetitive price; conventional crops could not meet the potential global demands for biofuels to counteract declining fossil fuel reserves, mainly because of potential competition with food and feed markets, which also generates widespread social controversy (Sarkar et al. 2012).

Edible crops provide a high sugar content, which in turn leads to increased production yields of sugar-derived products (e.g. bioethanol). The challenge for first-generation biorefineries is to be able to exploit crops without causing potential damage to food security, arable land or land-use change (Gnansounou and Pandey 2017).

1.1.2 Second Generation Biorefineries

Agro-industrial residues, non-edible crops and forestry products present opportunities to avoid the use of food-based feedstock in biorefineries. Within the scope of second-generation biorefineries, different raw materials such as grass, straw, hemp, forest biomass or harvest residues from crops can be included (Stuart and El-Halwagi 2014).

The reuse of crops that produce woody by-products or crops not intended for food production avoids a speculative increase of food prices (Hatti-Kaul 2010). Current research trends focus on the lines of lignocelluloses and feedstocks that provide lignin, hemicellulose and cellulose. Barriers related to fractionation of lignocellulosic biomass, energy needed for product separation, biological and chemical inhibition and better integration of the entire process chain should be considered (E4tech et al. 2015). The opportunities arising from the use of unprofitable fractions of lignocellulosic biomass make it possible to increase the intrinsic value of the raw material by producing several high added value chemicals.

Second generation biorefineries go beyond the use of food as fuel. However, one of the potential challenges faced by this category of biorefineries is the potential diversion of arable land use from food production to energy production. Such is the case of energy crops, an option that avoids the use of food as a raw material for bioenergy production, but requires land-use change (Harris et al. 2015).

To avoid this concern, a conceivable option would be to transform biomass fractions that have a minimal impact on the use of water, fertilizers, herbicides, machinery, as well as land-use change. Lignocellulosic by-products or waste fractions from crop cultivations that would have no other application are some potential examples (Tomei and Helliwell 2016).

Pretreatment of Lignocellulosic Biomass as an Essential Requirement

Within the European framework, second-generation biorefinery, also known as lignocellulosic biorefinery (LCB), uses wood (including forest residues and black liquor) and straw as main feedstocks (Biorefinery Euroview 2008). The transformation process in an LCB consists of four main steps: pre-treatment, hydrolysis, fermentation and product purification. In its natural state, lignocellulosic material is difficult to be treated by direct hydrolysis of cellulose into glucose. Therefore, the fractionation of lignocellulosic biomass is one of the most complex operations among biorefinery processes, mainly due to the structure of solid and interconnected cell walls of biomass. The complex polymer structure of cellulose and the integrated base of hemicellulose and lignin tend to obstruct and prevent its conversion into monomeric sugars (Kamm and Gruber 2006).

Based on these factors, it is necessary to develop effective pre-treatment stages to reduce the size of material particles and alter their cellular structure to make it more accessible to chemical or enzymatic hydrolysis processes (Himmel et al. 2007). These processes can be based on mechanical, physical, chemical and/or biological treatments.

The selection of the pre-treatment method plays a critical role in the transformation of lignocellulosic biomass in a viable and cost-effective way (Kautto et al. 2013). Several pre-treatment methods have been studied and in general, this step has been considered one of the most costly processes in the conversion of lignocellulosic material (Harmsen et al. 2010). All pretreatment techniques can be classified into four different groups, as depicted in Table 1. The main objectives of pretreatment technologies are to improve the yields of hexoses and pentoses in downstream processing by ensuring lignin recovery, decrease costs in size reduction of biomass, minimize energy and chemicals requirements, be flexible enough to process different lignocellulosic feedstock and reduce waste production (Alvira et al. 2010).

Table 1 Lignocellulosic biomass pretreatments Adapted from Prasad et al. (2016)

Pretreatment category	Methodology
Physical	Wet milling
	Dry milling
	Grinding
	Microwave
Chemical	Alkaline hydrolysis
	Acid pretreatment
	Organosolv process
	Ozonolysis process
	Wet oxidation
Biological	Fungal degradation
Physicochemical	Steam explosion
	Ionic liquids
	Catalyzed steam explosion
	Ammonia fiber explosion
	Liquid hot water

Going Deep into Lignocellulosic Biorefineries: Organosolv Process

Among the pretreatment techniques for wood fractionation, organosolv pretreatment has been found to have the advantage of using solvents that can be easily recovered while obtaining high quality lignin (Alvira et al. 2010). During the process, an organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4) is used to break down the internal structure of lignin and hemicellulose. The most common organic solvents used are methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol (Chum et al. 1988). Organic acids can also be used as catalysts during the process; however, at high temperatures (above 200 °C), the addition of catalyst is unnecessary for delignification (Aziz and Sarkanen 1989) but leads to a high yield of xylose. Once the reaction is complete, it is necessary to recover the solvent for reuse, as it may inhibit the subsequent stages of enzymatic hydrolysis and fermentation.

Its use as a fuel for heat and electricity production are common applications of the large amounts of lignin generated in pulping processes (Kleinert and Barth 2008). Recent studies have shown that due to its high quality, organosolv lignin offers different applications as a substitute for phenolic resins or polyurethane compounds (Pandey and Kim 2011). Besides lignin, many other co-products can be recovered from the main stream of hemicellulose, including sugars, acetic acid and furfural. Cellulose and hemicellulose can be hydrolyzed enzymatically to C6 and C5 sugars. These sugar flows can be further fractionated, offering opportunities for the production of biofuels and bio-based chemicals (E4tech et al. 2015).

Although the use of organosolv as a pre-treatment may benefit the production of co-products, its practice has been assumed to be more complex and costly than other methods, due to the high energy consumption in distillation and safety costs and the potential risks of fire and explosion (Zheng et al. 2009). In views of cushioning the high costs of production of organosolv pulp, an attempt should be made to recover all possible products at subsequent stages of processing.

1.1.3 Third Generation Biorefineries

Third generation biorefineries use aquatic biomass such as algae to produce, mainly, biodiesel or vegetable oil due to their high oil content (Faraco 2013). Algae and microalgae are considered a very promising feedstock as they require CO_2 for their growth, which can counteract GHG emissions. Moreover, this feedstock does not compete directly with other crops for arable land, as it is grown in photobioreactors or raceway ponds (Gavrilescu 2014).

Algae growth rates and reactor design should be optimized to maximize production; optimized production would allow efficient conversion to protein, carbohydrates and lipids. However, the bottleneck of marine biorefinery is the harvesting and subsequent extraction. The potentiality of third-generation biorefineries is increasing, due to the multiple efforts towards technological advances, as well as the possibility of not only producing biodiesel, but also other products such as ethanol, hydrogen, liquid fuels, methane and high value products (pigments, antioxidants, carotenoids, proteins). In terms of sustainability, algae biorefineries present strengths over the feasibility of reusing nutrient-rich wastewater instead of saline water (Martín and Grossmann 2013).

1.1.4 Fourth Generation Biorefineries

Some authors propose the inclusion of an additional category of biorefineries for those systems that exploit raw materials that do not belong to any other category (Demirbas 2010; Gavrilescu 2014; Haddadi et al. 2017; Stuart and El-Halwagi 2014). In the case of fourth-generation biorefineries, the main feedstocks are waste fractions, such as municipal waste. These biorefineries follow a circular economy approach, using waste that is difficult to manage and has the potential to produce biofuel.

Fourth-generation biorefineries potentially include facilities for the treatment of feedstocks that are not directly related to crop cultivation, use of arable land or production of marine feedstock. Rather, they are intended for the valorization of waste fractions such as those from vegetable oils, food industry and even sewage sludge. These new-generation biorefineries may not follow the standard structure of a biorefinery plant and may be combined with wastewater treatment plants or industries to produce valuable products from waste and therefore manage such waste on-site (Haddadi et al. 2017). An example of the fourth-generation biorefinery concept is the production of polyhydroxyalkanoate from primary and secondary sludge in wastewater treatment plants (Morgan-Sagastume et al. 2014; Mosquera-Corral et al. 2017).

1.2 Biorefinery Configurations Attending to Products

Some biorefineries have fixed processes and produce a fixed amount of ethanol and other end products, while other configurations can produce multiple end products. The flexibility of the plant to use a blend of biomass feedstocks influences the possibility to produce a variety of products by combining technologies (Kamm and Kamm 2004).

One of the objectives of a biorefinery is to obtain products in concentrations that make purification or recovery economically feasible (Mosier et al. 2005). In fact, some authors (Boisen et al. 2009) argue that a biorefining facility should not be limited to the production of a single high value added bioproduct and that bio-based raw materials should be used as efficiently as possible.

Therefore, we can find that a wide range of bio-based products can be obtained depending on the production targets of the biorefinery and technology readiness level (TRL) of the downstream processes. On the other hand, the layout of the plant may vary depending on whether the main production objective is to obtain mainly bioenergy/biofuels or high added value products. In any way, biorefineries are viewed, in most cases as complex systems with multi-production perspectives. Not all plausible products that can be obtained from the biorefinery route have equally developed TRL, the same market size or equal potential market forecasts. Listed below are some of the possible products manufactured in biorefineries (E4tech et al. 2015).

- Basic bio-based building blocks. Lignin, hemicellulose, cellulose, glucose, fructose, galactose, xylose, arabinose, ribose, lactose, sucrose, maltose.
- Platform and fine biochemicals. Methane, formic acid, ethanol, acetic acid, glycolic acid, lactic acid, propionic acid, succinic acid, xylitol, levulinic acid, furfural, hydroxymethyl furfural (HMF), citric acid, furandicarboxylic acid (FDCA), lipids, 1,4-butanediol, ethyl acetate, cyrene.
- Biopolymers. Polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polystyrene (PS), polyhydroxyalkanoates (PHA).
- Biomaterials. Foams, composites, bioplastics and films (manufactured from biopolymers).
- Biofuels/bioenergy. Gasoline, jet fuel, diesel, alkanes, biogas.

1.3 Biorefinery Under the Focus of Sustainability

Recently, several studies have performed an environmental evaluation of biorefinery systems. Although most of them have confirmed that bio-based products present lower environmental burdens than fossil-based products, a new concern is the wide range of biomass feedstock alternatives and emerging technologies for conversion, from which the most environmentally friendly should be chosen for future biorefinery processes (Stuart and El-Halwagi 2014).

Life Cycle Assessment (LCA) is a methodology for assessing the potential environmental impacts and resources consumption associated with a product or production system throughout its life cycle, as well as identifying opportunities for environmental benefits (ISO14044 2006a, b). Different environmental assessment studies have been carried out on biorefinery systems. However, it is difficult to compare their results because they have considered different feedstocks, technology treatments, system boundaries or methods of environmental allocation.

González-García et al. (2011) identified and quantified the environmental impacts associated with a Swedish softwood-based biorefinery where total chlorine-free (TCF) cellulose, ethanol and lignosulfonates were produced. They have found that the production of chemicals consumed in the cooking and bleaching stages, the treatment of sludge generated in the wastewater treatment plant and the on-site energy production system were the elements that contributed most negatively to environmental burdens. Hernández et al. (2014) studied an olive stone based biorefinery and carried out an environmental assessment of two biorefinery schemes describing the integrated production of xylitol, furfural, ethanol and a cogeneration system to produce bioenergy from solid waste. The results showed that for both biorefinery schemes, there were considerable net profit margins. Regarding the environmental analysis, they concluded that the cogeneration system reduced energy consumption.

Laure et al. (2014) assessed an organosolv lignocellulose biorefinery at pilot plant scale, highlighting the benefits of a lignocellulose biorefinery and the importance of valorizing all the fractions obtained in order to create a competitive bio-production. Budzinski and Nitzsche (2016) evaluated four conceptual beech wood based biorefineries. The results indicated that the four biorefinery systems had fewer total potential environmental impacts than fossil-based reference systems. González-Garcia et al. (2016) highlighted the relevance of multi-product valorization when considering the environmental performance of biomass refining into high-added value compounds.

1.4 Energy Security

The European Commission, on the Energy 2020 Strategy (European Commission 2010), defines energy security as the uninterrupted physical availability of energy products on the market at an affordable price for private and industrial consumers, while contributing to the EU's social and climate objectives. Europe energy policies base the main objectives to be achieved by 2020 on ensuring security of energy supply, competitiveness and sustainability. The sustainability objective is based on the development of environmental quality systems that produce energy from renewable sources. The concept of energy security can therefore be closely linked to the sustainability of biorefinery systems.

In the case of biorefineries producing biofuels, sustainability is addressed, for example, by exploiting feedstocks mentioned in Sect. 1.1. Moving towards a biotechnology-based economy is an opportunity to achieve the established targets for energy security in Europe. The strategic objectives provide an alignment towards decarbonizing energy sources, giving priority to renewable energies, supplying and using energy efficiently and improving energy technologies and innovations (European Commission 2010).

2 Life Cycle Assessment of Biorefinery Schemes

Life cycle assessment is a tool that has been widely used to report environmental sustainability criteria of biorefineries for the production of bioenergy (Li et al. 2018) and bioproducts. Biorefineries are inherently characterized by their flexibility, as seen in Sect. 1, they offer a wide range of possibilities. Thus, the results derived from LCA may be divergent when assessing different types of facilities.

The functional unit, objective and scope, system boundaries and method of each individual study affect the overall results reported on LCA. This section aims to conduct a review of biorefinery LCA studies on literature to evaluate the overall profile of different biorefinery schemes and to assess the relative implications on issues such as the relevance of energy footprint. The state of the art regarding the life cycle assessment of biorefineries can be described through the sample of studies presented in Table 2. The sample includes 31 peer-reviewed papers that are considered representative of research from the last decade.

2.1 Goal and Scope Definition

The definition of the goal and scope in LCA should be clearly stated, providing the intended application and reasons for conducting the assessment, the functional unit, the system boundaries and inventory data (ISO14044 2006a, b).

Among the reviewed papers, 52% were studies on second generation biorefineries, 24% on first generation biorefineries, 18% on third generation biorefineries and finally 6% on fourth generation biorefineries. This clearly indicates that the research trends have been focused on the valorization of lignocellulosic materials. Second generation biorefineries take a relevant share, lower however than first generation biorefineries, which are far more implemented industrially on a real scale. Studies on valorization of algae and municipal solid waste are far from being adopted industrially since they are in the early stages of technological development at laboratory or pilot scale.

In terms of products of interest for each configuration, the conclusion is that biorefineries tend to be more sustainable or economically viable, either in the production of energy and biofuels or energy/biofuels together with bioproducts. Of the documents reviewed, 68% considered the production of biofuels and/or electricity along with one or more bioproducts. In contrast, 19% and 13% considered the production of biofuels/bioenergy or of bioproducts exclusively, respectively.

2.1.1 Functional Unit

The functional unit (FU) provides a reference to which input and output data are normalized, it should be mathematically measurable. The functional unit should be carefully selected to allow comparisons between the valorizing systems under study (ISO14044 2006a, b). Attention should be paid to the selection of FU since decision-making strategies may depend heavily on it. Based on the literature review, one quarter of the studies have selected a FU referred to the feedstock, while the remaining three quarters have chosen a FU related to the products.

Feedstock-based functional units include volumetric or mass values (16% of reviewed documents) and hectares of land (9%). Among product-based FU, the variability is greater. 35% of the papers have chosen a FU that represents the

Table 2 Literature review of LCA biorefinery studies

References	Feedstock	Products	Functional unit	System boundary	Data quality	Method	Environmental categories/ indicators	Energy indic.
Adom and Dunn (2017)	Corn Corn stover Glucose	Polymer grade lactic acid Ethyl lactate	kg product	C-G, C-GR	2, 3, 4	GREET	GHG	FEC
Arodudu et al. (2017)	Maize	Ethanol Biogas	ha of land	C-G	2, 3	–	–	NEG EROEI
Barlow et al. (2016)	Algae	Biofuel	1 MJ of fuel	W-P	2,3,4	–	GWP	NER
Collet et al. (2014)	Microalgae	Methyl ester Glycerin	1 MJ methyl ester	C-G	2	ReCiPe	CC, OD, HT, FET, MET, POF, PMF, IR, FET, ME, FE	CED
Escamilla-Alvarado et al. (2017)	Municipal solid waste	Hydrogen Methane Holocellulases Hydrolysates	1 ton municipal solid waste (20% total solids)	G-G	1, 2, 3	CML 2001	AD, AP, EP, GWP_{100}, OD, POP	–
Farzad et al. (2017)	Sugarcane residues	Ethanol Lactic acid Furfural Butanol Methanol Electricity	65 tons residues/h processed at the biorefinery	C-G	2, 3, 4	CML-IA baseline	AD, GWP, AC, EU, ODP, POCP, HT, FET, TEC, WC, WS	SED
Fiorentino et al. (2014)	Brassica Carinata	Ethyl levulinate Formic acid Glycerin Biodiesel Lignin Electricity	1 ha of marginal land with B. carinata	C-G	1, 2, 3	CML 2001	AD, AC, EU, GWP, HT, PO	CED

(continued)

Table 2 (continued)

References	Feedstock	Products	Functional unit	System boundary	Data quality	Method	Environmental categories/ indicators	Energy indic.
Giwa (2017)	Algae and Cattle manure	Biogas Energy	1 GJ biogas/year	C-GR	2, 3	Eco-indicator 99	Carcinogens, respiratory organics and inorganics, radiation, ecotoxicity, land use, minerals, fossil fuels, CC, OD, AC, EU	–
Gnansounou and Raman (2016)	Algae	Biodiesel Glycerol Animal feed Succinic acid	1 km	W-WH	2	ReCiPe	GHG, land use	FEU
Gontia and Janssen (2016)	Pulp mill residual streams	Sodium Poly-acrylate Ethanol	1 kg sodium poly-acrylate	C-G	1, 2, 3	CML	GWP, EP, AP, POCP	REU NREU
González-García et al. (2011)	Softwood	Lignosulfonates Ethanol	1 ton air-dried (10% moisture) dissolving cellulose from pine and spruce	C-GR	1, 2, 3	CML-2 baseline 2000	AD, GW, OD, HT, FE, ME, TE, PO, AC, EU	–
González-García et al. (2016)	Residual wood	Cellulose Lignin Monosaccharides Hemicelluloses Levulinic acid Formic acid	1 € revenue	C-G	1, 2, 3	ReCiPe	CC, OD, TA, FE, ME, HT, POF, TEC, FEC, MEC, WD, FD	–

(continued)

Table 2 (continued)

References	Feedstock	Products	Functional unit	System boundary	Data quality	Method	Environmental categories/ indicators	Energy indic.
Khoshnevisan et al. (2017)	Castor	Biodiesel Ethanol Electricity Methane Glycerol K_2SO_4	1 GJ output energy from combustion of castor biodiesel blend	W-WH	2, 3	IMPACT 2002+	Resources Human Health Ecosystem quality	NEG FER
Kim and Dale (2015)	Corn stover	Ethanol Electricity	1 MJ ethanol	C-G	2, 3	GREET	GW, AC, EP, SMG, OD, EC, PM, HHC, HHNC	FEU
Levasseur et al. (2017)	Hydrolysate in Kraft pulp mill	Ethanol Butanol Acetone	1 kg butanol	C-G	2, 3	IMPACT 2002+	Resources Human health Ecosystem quality	–
Lin et al. (2015)	Lignocellulosic Biomass	Glucose Hemicelluloses HMF Levulinic acid 2,5-hexanedione Xylene	1 ton p-xylene	C-G	2, 3, 4	ReCiPe	OD, HT, EC, IR, POF, PMF, CC, TET, TA, ALO, ULO, NLT, MET, ME, FE, FET, FD, MD, WD	–
Mandegari et al. (2017)	Bagasse Brown leaves	Glucose Xylose Electricity Lactic acid Ethanol	1 ton lactic acid	C-G	2, 3, 4	CML-IA Baseline	AD, GWP_{100}, AC, EU, OD, POCP, TET, FET, HT	SED
Modahl et al. (2015)	Timber Wood chips	Ethanol Cellulose Lignin Vanillin	1 ton product 1 m^3 ethanol	C-G	2, 3	CML 2 Baseline 2000 IPPC 2007	CC, AC, EU, POF, OD	CED

(continued)

Table 2 (continued)

References	Feedstock	Products	Functional unit	System boundary	Data quality	Method	Environmental categories/ indicators	Energy indic.
Moussa et al. (2016)	Sorghum	Succinic acid $(NH_4)_2SO_4$	1 kg succinic acid (99.5 wt%)	C-G	1, 2, 3	IPPC 2007	GWP_{100}	CED SED
Ofori-Boateng and Lee (2014)	Oil palm fronds	Ethanol Phytochemicals	1 ton anhydrous ethanol (99.15 wt %)	C-G	2, 3	CML 96	AP, AETP, EP, GWP, HTP, ODP, POCP, TETP	EIP
Olofsson et al. (2017)	Agricultural crop residues	Ethanol Electricity Lignin	1 MJ bioethanol (LHV)	C-G	2, 3	Renewable energy directive (RED)	GWP	Primary energy
Parajuli et al. (2017)	Wheat straw Alfalfa	Ethanol Lactic acid Electricity	1 MJ ethanol (99.5 wt%) and 1 kg lactic acid	C-G	2, 3	ReCiPe	GWP_{100} with and without ILUC, EP, ALO	NRE
Pereira et al. (2015)	Sugarcane	Ethanol Acetone n-Butanol Electricity Sugar	kg butanol US$ earned km run by car	C-G	2, 3, 4	CML 2 Baseline 2000	AD, AC, EP, GW, HT, PO	–
Rahimi et al. (2018)	Eruca sativa	Biodiesel Electricity Ethanol Heat Glycerol Biomethane	1 GJ output energy from biodiesel	W-WH	2, 3	IMPACT 2002+	Resources, human health, ecosystem quality	NEG FER
Raman and Gnansounou (2015)	Vetiver leaves	Lignin Ethanol Furfural	1 km passenger travel operated on ethanol	W-WH	2, 3	ReCiPe	CC, FD	–

(continued)

Table 2 (continued)

References	Feedstock	Products	Functional unit	System boundary	Data quality	Method	Environmental categories/ indicators	Energy indic.
Seghetta et al. (2016)	Seaweed	Bioethanol Fertilizer Fish feed	1 ha of sea under cultivation	C-GR	1, 3, 4	ReCiPe	CC, ME, ME-Plim, HT-C, HT-NC	CED-T CED-F
Silalertruksa et al. (2015)	Sugarcane	Bioethanol Biogas Sugar Electricity	Unit of product	C-C	1, 2, 3	ReCiPe	GHG emissions, GVA	–
Souza et al. (2015)	Sugarcane Algae	Biodiesel Ethanol Algae meal Electricity	1 MJ hydrous ethanol	C-G	1, 2, 3	Monte Carlo simulation	GHG emissions	FEU
Tao et al. (2014)	Corn Stover	Isobutanol Ethanol n-Butanol	1 km travelled by a flex-fuel car operated on biofuels	F-WH	3, 4	-	GHG, EROI, CAPs	FEU NEV
Uihlein and Schebek (2009)	Straw from agriculture	Xylite Lignin Ethanol	1 kg ethanol	C-G	2, 3	Eco-indicator 99	Human health, resources and ecosystem	–
Vaskan et al. (2018)	Palm empty fruit bunches	Ethanol Animal feed Electricity	1 ton empty fruit bunches	W-WH	3, 4	ReCiPe	CC, FD, HT, FET, FE & economic indicators	–

1 Primary data, 2 literature data, 3 databases, 4 modelling/simulation, C cradle, G gate, GR grave, W well, WH wheel, F field, P product

quantity of product, either in mass or volumetric values, with units such as kg, ton, m^3, L. Close follows 28% of the papers that have opted to use a FU referred to energy, with units such as MJ or GJ of energy produced in the form of biofuels or electricity. The distance travelled by a car fueled on biofuel is a relatively common FU, although only 9% of the reviewed studies have worked with it. Finally, only 3% of the studies have used the monetary benefit as a reference unit.

The functional unit should not only represent a number and a unit. It involves the specific circumstances of the study under which such number and unit make sense. For instance, some of the reviewed papers refer to a time frame, geographical location or composition value.

2.1.2 System Boundaries

The system boundary describes all the unitary processes included within the system evaluated through LCA. The stages and boundaries selected for the study, as well as the omissions considered, should be identified and explained. It is helpful to describe the systems using process flows diagrams that show where the unitary process begins with raw materials and ends with the management of the final products (ISO 14044 2006a, b).

A large portion of the reviewed papers (59%) have studied the process from the feedstock production to the final products at the plant gate (cradle to gate). A slightly broader scope has been adopted in 13% of papers, including the disposal phase (cradle to grave). The well-to-wheel system boundary is a common scope used for studies related to the production of biofuels for vehicles, considered in 16% of the studies. It is important to note that the selection of system boundaries may be influenced by the availability of data on issues such as end-of-life or waste management.

2.1.3 Inventory Data

Inventory data of studies provides the basis for an environmental evaluation that may be representative of specific processes or products. Data quality and completeness of inventories influence the reliability of the life cycle assessment results. This review compiled sources of inventory data. Almost all studies consider a combination of different sources to ensure completeness of inventory gaps. For instance, when primary data is available, background process data is often implemented through literature or database information.

Regarding biorefinery systems, most of the data is obtained from literature and databases (38 and 39% respectively), being Ecoinvent one of the most common databases. Primary, pilot facility or large-scale data are very rare (11%), as is the use of inventories from modelling or simulations, which account for 12% of the data retrieved in reviewed studies.

2.2 Method and Impact Categories

The method selected to perform the environmental evaluation determines the characterization factors and model that represent the aggregated impacts of inputs and outputs. The method is usually implemented through specialized software and provides a set of impact categories as for the collective description of results (ISO 14044 2006a, b). The most commonly used methods among the reviewed papers were CML in its different versions (IA Baseline 2000, 2002) and ReCiPe. In general, both these methods were applied in two-thirds of the studies.

Among the impact categories, the most frequently used was global warming potential in all its variants (climate change, greenhouse gas emissions). In fact, studies often focused exclusively on determining this environmental category through the calculation of kg CO_2 of input and output flows. Other set of indicators that were relevant for the evaluation of biorefineries were ozone depletion, acidification, eutrophication and toxicity.

Due to the relevance of energy consumption and the feasible production of bioenergy in biorefineries, the study of energy indicators on biorefineries is relevant. Some of the revised documents have considered energy-related indicators. Of 31 studies, 20 used at least one indicator representing energy consumption or production. The most common indicators were the net energy gain (NEG), cumulative energy demand (CED), specific energy demand (SED) and fossil energy use (FEU). Overall, the evaluation of the energy footprint of biorefineries has certainly not been studied to the point of accomplishing environmental optimization of energy-related procedures.

Conclusively, LCA studies on biorefinery systems should typically address some key features and methodological assumptions. Life cycle assessment is a discipline in which the main goal is to analyze environmental performance of a process. However, many times, the study of the environmental performance of a process does not show environmental excellence by its very nature. Upon analysis of the presented overview, the goal of LCA, particularly in novel processes should not only be to provide environmental results of a process but to establish a benchmark for comparison with reference systems or with different processing routes.

The optimality of a life cycle assessment study is determined by the nature and quality of the available data. The scope of the study should cover the areas in the value chain in which data is available and reliable. If data is available, it is advised that the feedstock production is included within system boundaries, since it represents one of the most characteristic distinctives of biorefinery systems, which is the exploitation of biomass with the purpose of providing biofuels and biochemicals.

According to the literature review, the variability on the selection of functional unit is high. This, again, is highly impacted by the type of system under study. When the biorefinery system clearly has a wide range of products in their portfolio, and there is not one that can be highlighted as the main product (according to production volume, economic relevance, etc.), the suggestion on the selection of functional unit is to favor feedstock-based reference units. If the target, however, is to evaluate the energy footprint of biorefinery scenarios, it may be more appropriate to define a functional unit referred to the output energy/fuel production, for instance, 1 MJ of fuel. If the aim of the study is to describe a system up to the use of a biofuel-powered vehicle, then is coherent to adopt functional units that include the vehicle's features (e.g. efficiency), for example 1 km travelled in a specific vehicle powered by the produced biofuel.

Finally, with respect to the selection of impact categories and indicators, typically, LCA studies have followed the trend of focusing on carbon emissions. However, considering the potential nature of diverse processes in the biorefinery field, it is advised that at least one indicator is included out of categories such as ozone depletion, acidification, eutrophication and toxicity. It has been observed that energy-related indicators such as NEG, CED, SEG, etc. act as fair descriptors of biorefinery systems, in terms of sustainability, percent use of fossil resources or energetic efficiency.

3 Biorefineries in Europe. State of the Art

The theoretical vision of biorefineries in literature has been revised continuously in one or another way. As it has been mentioned, many research studies have analyzed environmentally biorefinery related processes. There are, as well, plenty of research studies that evaluate and analyze the production of biochemicals, or biofuels, mostly at laboratory scale. However, the best overall vision that one could have in the field of biorefineries, is through an analysis of existing biorefining facilities. For the purpose of this study, the search of facilities has been narrowed down to European facilities producing biofuels, bioenergy or bioproducts. Through the evaluation of common characteristics in existing biorefineries, the expected result is to obtain an overview of the state of the art and future possibilities and prospects in the field of sustainable processing.

A total of 568 biorefinery facilities were reviewed throughout Europe in available databases and compilations (Bioenarea 2010; Biorefinery Euroview and Biopol 2009; E4tech et al. 2015; IEA Bioenergy 2018; Nova Institute and Consortium 2017). In this chapter, different types of production plants were considered. The scope includes processing plants to obtain bioethanol, biodiesel, bioproducts as well as power plants that use coal and biomass blends as fuel. The first objective was to analyze which were the European countries with highest density of biomass transforming facilities. Figure 3 displays a density map featuring reviewed biorefining facilities. From the evaluated group of biorefineries, Germany was the country with more biomass processing plants, with a total of 132. Finland was found to be quite relevant as well, with 102 plants. Other countries such as Italy, Denmark, France, The Netherlands, Sweden and United Kingdom were found to have an intermediate number of facilities, ranging from 23 to 55 factories. Spain, Ireland, Hungary, Czech Republic, Norway, Poland, Portugal, Slovakia or

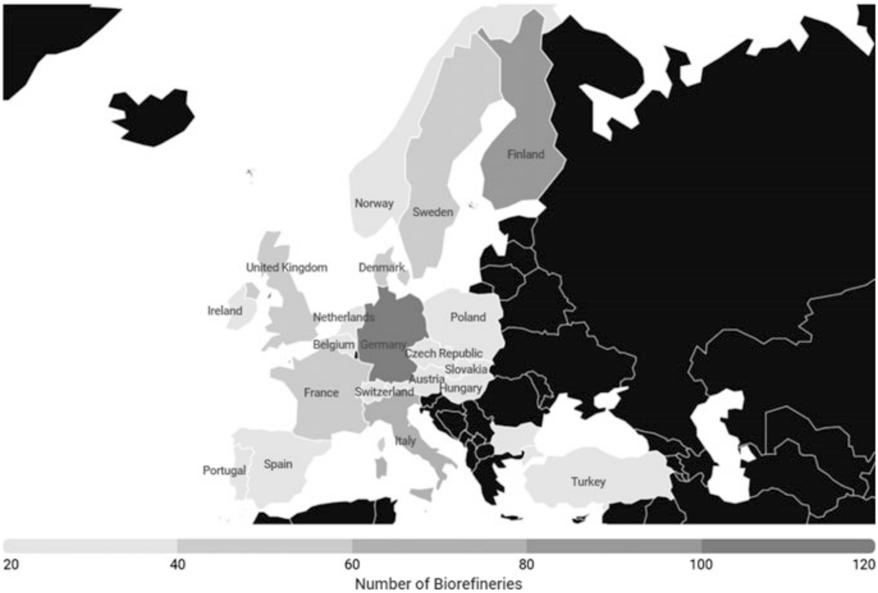

Fig. 3 Density map of European biorefineries

Switzerland were countries with less than 17 reported biorefineries. By all means, the list of reported biorefineries may not be completed to its fullest, however, it can be considered as a good approximation of the trends in Europe.

Among biorefinery studies, one of the most relevant concepts used to acknowledge the level of development of a process is the technology readiness level (TRL). This indicator can be used as a way of expressing maturity and development levels of technologies and innovative processes (Fig. 4). An approximated evaluation of the TRL of reported biorefineries has resulted in 82% of facilities with technology readiness levels of 8–9. Lower TRL of 6–7 and 4–5 were present in 9 and 8% of the cases respectively. The remaining 1% corresponds to biorefineries with technology readiness levels in the range of 1–3. With this, it can be stated that among reported biorefineries, most of them are considered to have technologies in operational environments that are considered to produce bioproducts and/or biofuels to a commercial level. The conclusion that can be drawn from this information is that biorefineries producing some kind of value-added product (in the form of materials or energy) in Europe are considered to have up-to-date or mature technologies. This in turn may signify that the development of bioprocesses in Europe is mainly centered towards processes that have been available for years now, rather than incurring in novel processes to produce specialty chemicals through innovative technologies. This would mean that Europe needs to take a step towards the development of researched processes in laboratory level and scale them to pilot or demo operations, to avoid stationary knowledge.

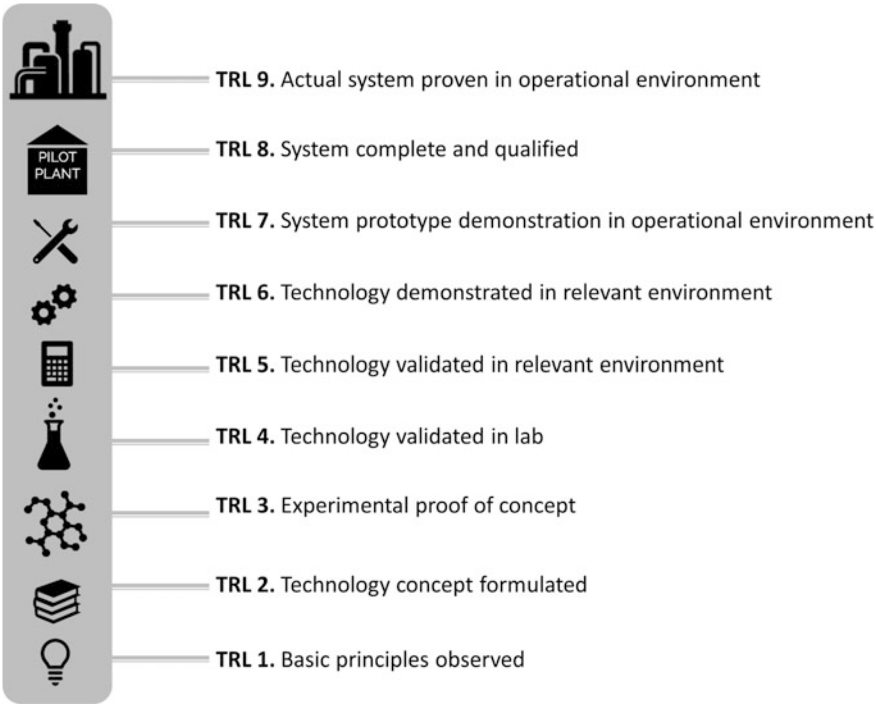

Fig. 4 Technology readiness level (TRL) diagram

Regarding the feedstock used in the considered biorefineries, the most frequent type of raw material was the category that englobes lignocellulosic materials. Around 38% of the reviewed facilities were englobed under the second generation biorefinery category. Under this group of feedstocks, the raw materials that could be frequently encountered along the different types of facilities were sawmill residues such as woodchips, bark or sawdust as well as residual crop fractions such as straw or grass. About 35% of facilities were plants that use blends of biomass with coal and peat. These were mostly power generation plants producing electricity and heat by means of burning biomass and coal. With less frequency, first generation biorefineries were identified (13%). Some of the most popular feedstocks within this category were wheat, corn, sugar beets and oil crops (rapeseed, sunflower, palm, soybean, kernel, coconut). Regarding fourth generation biorefineries, approximately 7% of processing plants were assigned to this group in the performed review. As defined in this study, fourth generation biorefineries are processing facilities that use as raw materials mostly residual fractions. Within the residual fractions available to be used as feedstock, some were sewage sludge, residual cooking oils, whey, manure and sulfite spent liquor streams from the pulp and paper industry. The remaining 7% of facilities were plants with possibilities to process different types of feedstock. These were usually combinations of raw materials from the different categories (first, second and fourth generation feedstocks). For instance, some facilities considered the use of blends of used oil, cooking oil and other residual fat and oil streams together with oil derived from oilseed crops. These biorefineries are usually intended to produce biodiesel and/or oleochemistry products such as fatty acids, glycerin, fatty alcohols, fatty amides, fatty esters, surfactants, methyl esters, paraffin waxes etc. It can be observed that biorefineries tend to use feedstocks that are commonly harvested or produced (as residues or as crops) nearby.

Very few times existing biorefineries were found to have the objective of producing fine chemicals such as furfural, levulinic acid, hydroxymethyl furfural or base chemicals as precursors of bio-based polymers or other chemicals. The reviewed plants are mostly producers of bioethanol, biodiesel, electricity and heat with little or no mention on the possibilities for recovery of side-stream bioproducts that would be feasible to be recovered alongside ethanol, sugar and pulp production processes.

4 The Energy Consumption Profile of a Biorefinery. LCB Case Study

Biorefineries have not being widely implemented at full scale, in fact, it is not yet possible to study issues such as energy integration on the basis of primary results. It is accurate to assert that the study of lignocellulosic biorefineries has been approached by literature in different ways.

The purpose of this study is to determine the impact of energy consumption in biorefinery facilities on environmental issues such as sustainable bioenergy production (in the form of bioethanol). The environmental study of a lignocellulosic biorefinery is presented as a case study to elucidate which would be the main impacts derived from the energy needs of a modelled facility with specific production characteristics. The intention of the LCA study is to provide an overview of the process areas and impact categories that are environmentally burdened by energy-related systems (energy consumption and energy production).

4.1 Materials and Methods

4.1.1 Goal and Scope

As mentioned before, LCA is a technique for assessing the potential environmental impacts associated with a product or process (ISO14044 2006a, b). The aim of this study is to assess the environmental performance of a lignocellulosic feedstock biorefinery by means of LCA methodology, considering the simulation work of

Kautto et al. (2013). The lignocellulosic biorefinery (LCB) produces high-added value products from residual woody biomass (waste stream from forest activities). The principles established by the ISO standards (ISO14040 2006; ISO14044 2006a, b) and the ILCD handbook (European Commission 2010) were followed in this research study. The functional unit considered for the assessment was the processing of 1 t/h of hardwood chips in the plant described in Sect. 4.1.2.

4.1.2 System Overview

Under the LCA approach, the analysis of a process should include defining clear boundaries and the processes within those boundaries that are required to be evaluated. In this study, the analysis of the biorefinery under assessment was carried out from a cradle to-gate perspective, considering the extraction of raw materials to produce the required products, but not the final disposal stage. All the activities involved, from the production of the raw materials to the final valorization processes of high-added value products in the biorefinery, were considered within the system boundaries, following the guidelines from other biorefinery works such as González-García et al. (2016), Laure et al. (2014) and Budzinski and Nitzsche (2016).

For the sake of clarity, the biorefinery was divided into subsystems (SS), which will be analyzed as independent blocks that compute to the total environmental impacts. The definition of different subsystems in the process makes it possible to identify the areas of the plant that represent a clear environmental burden for the entire system. Figure 5 shows a simplified block diagram of the production process and the identification of the main flows and subsystems.

The selected biomass to be exploited was hardwood chips, as a residual stream from a sawmill. The impacts associated to the raw material primary operations (SS0) in the sawmill were exclusively considered as the percent impacts directly related to the retrieval of the residual wood chips (González-García et al. 2014). This is made possible by implementing an economic allocation to the main product fractions in SS0 (bark, wood and wood chips).

Organosolv is a feasible pre-processing step to fraction lignocellulosic material. The organosolv process (SS1) of the system under study is based on the fractionation of beech wood at 180 °C for 60 min with ethanol and water (1:1 w/w) and 1.25% sulfuric acid as a catalyst. The delignification of wood through organosolv gives rise in two streams: liquor and pulp.

Subsystem 2 (SS2) includes all processing units that condition the liquor fraction and allow the recovery of the main non-energy based bioproducts (acetic acid, lignin and furfural). The liquor is mainly treated in a distillation column to recover the solvent (ethanol). The recovered ethanol is recycled back to SS1, resulting in a reduced fraction of the required fresh ethanol input. The reduction of the ethanol content favors lignin precipitation. Furfural is obtained as a co-product in a side stream of a distillation column that is still sent to a decanting unit (Kautto et al. 2013).

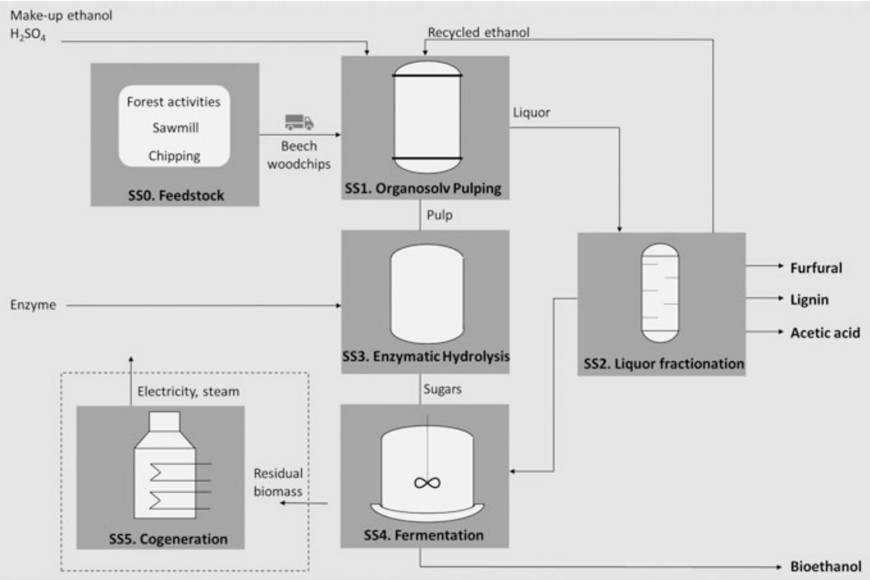

Fig. 5 Process diagram of the assessed wood-based biorefinery Adapted from Kautto et al. (2013)

After solvent recovery, water is evaporated from the liquor through a four-effect evaporation train. Evaporation allows low molecular weight lignin to be separated and burned as organic material in the boiler (SS5), along with other residual fractions. The resulting lignin-free hemicellulose fraction is used, together with glucose in the bioethanol fermentation (SS4). Acetic acid can be recovered from the condensates produced in the evaporation unit. Acid recovery is carried out through liquid-liquid extraction and distillation processes, with the use of trioctylphosphine oxide (TOPO) and undecane (Kautto et al. 2013).

The pulp or fiber fraction, washed with the ethanol-water solution before being discharged from the digester, is a cellulose rich fraction. The targeted objective for the pulp fraction is to transform the contained cellulose into second generation sugars, mainly glucose, which is performed in an enzymatic hydrolysis reactor (SS3), using an enzyme cocktail containing mainly cellulase. Cellulase production is considered within the system boundaries (Dunn et al. 2012; Heinzle et al. 2006). Cellulose hydrolysis is carried out at 48 °C for 84 h.

The resulting sugars in SS3 are further transformed in SS4, through fermentation by the microorganism *Zymomonas mobilis*. Bioethanol is recovered from SS4 with 99.9% purity by distillation and dehydration of the fermentation medium (Kautto et al. 2013).

The electricity and steam requirements of the biorefinery are covered through subsystem 5. This subsystem comprises the generation of the energy required to perform all transformation and valorization processes specifically considered in this case study. Subsystem 5 includes a boiler and a turbine for electricity production.

The boiler is designed to burn biomass waste from the process such as low molecular weight lignin, sewage sludge, bark and other organic residues. Natural gas is burnt to meet the energetic requirements of the plant (Kautto et al. 2013).

4.1.3 Life Cycle Inventory

The life cycle inventory stage in LCA is the collection of data regarding all material and energy inputs and outputs relevant to the system boundaries and scope of the study. The inventory data for this assessment has been taken from peer-reviewed bibliographic sources, such as the simulation results of Kautto et al. (2013) and González et al. (2014). Foreground processes have been addressed through the Ecoinvent database (Wernet et al. 2016). Table 3 presents the main inventory data for the system.

Table 3 Inventory for the lignocellulosic biorefining system defined for the functional unit of 1 t/h of residual beech wood chips including mass streams

SS0. Feedstock		
Overall inputs		
Diesel	1.03	kg
Fertilizer	0.15	kg
Water	244.38	kg
Chemicals	22.76	g
Packaging materials	0.27	kg
Lubricating oil	0.09	kg
Overall outputs		
Nitrogen emissions	52.68	g
Carbon emissions	30.77	kg
Emissions (SO_2)	0.82	g
Particulates	14.98	g
Municipal solid waste	1.50	kg
Residual woodchips	1.25	m^3
Bark	0.45	m^3
Sawn timber	1.8	m^3
SS1. Pulping		
Overall inputs		
Water	8.28	t
Sulfuric acid	1.01×10^{-2}	t
Ethanol	3.74	t
SS2. Liquor fractionation		
Overall inputs		
Water	1.02	t

(continued)

Table 3 (continued)

SS2. Liquor fractionation		
Ammonia	6.24×10^{-3}	t
Furfural (makeup)	1.92×10^{-3}	t
TOPO	3.32	kg
Undecane	11.93	kg
Overall outputs		
Acetic acid	1.56×10^{-2}	t
Furfural	5.28×10^{-3}	t
Lignin	0.16	t
SS3. Enzymatic hydrolysis		
Overall inputs		
Enzyme (cellulase)	7.80×10^{-3}	t
Cellulase production inputs (1 kg)		
Corn steep liquor	0.58	kg
Ammonia	7.82×10^{-2}	kg
Water	74.07	kg
Nutrients	0.32	kg
Cellulase production outputs		
N_2	0.28	g
O_2	0.84	g
CO_2	0.14	g
SS4. Fermentation		
Overall inputs		
Water	0.21	t
Corn steep liquor	1.27×10^{-2}	t
$(NH_4)_2HPO_4$	1.68×10^{-3}	t
Overall outputs		
Bioethanol	0.24	t
Water	0.37	t
CO_2	218.77	kg
O_2	1.44	kg
Wastewater	0.0034	m^3
SS5. Cogeneration		
Overall inputs		
Water	0.68	t
Sludge (WWT)	5.78×10^{-2}	t
Biogas (WWT)	4.27×10^{-2}	t
Natural gas	2.26×10^{-2}	t
Overall outputs		
CO_2	6.84	kg
Water (vapor)	108.84	kg

Table 4 Impact categories at midpoint level in the ReCiPe method analyzed in this study

Impact category	Acronym	Units of measure
Climate change	CC	kg CO_2 eq
Ozone depletion	OD	kg CFC-11 eq
Terrestrial acidification	TA	kg SO_2 eq
Photochemical oxidant formation	POF	kg NMVOC
Freshwater ecotoxicity	FET	kg 1,4-DB eq
Fossil depletion	FD	kg oil eq

4.1.4 Method

The environmental results were computed through the SimaPro 8.02 software by implementing the characterization factors from the ReCiPe 1.12 hierarchist method (Goedkoop et al. 2009). The evaluation of midpoint level impact categories was studied to determine the implications of the energy generation subsystem on LCA results. Although all categories of the ReCiPe method were studied, the environmental results are presented in terms of six impact categories relevant to the energy footprint in the system under study (Table 4).

The ReCiPe method has been popularly used in recent years on studies involving environmental assessment of biorefineries or biorefinery processes and includes impact categories that are considered to represent environmental characteristics of a system in a satisfactory manner (González-García et al. 2016; Lin et al. 2015; Parajuli et al. 2017; Silalertruksa et al. 2015). In this case study, selected categories have been targeted because of their relevance towards burdens from energy related activities.

4.1.5 Assumptions and Limitations

The limitations of the present study are mainly due to barriers on the data availability. For the studied system, mainly data from literature sources and databases has been utilized. Secondary data provides results with certain degree of uncertainty. In the same line, due to lack of available data, no infrastructure processes have been considered within the system.

4.2 Environmental Results and Discussion

The results of the environmental assessment indicate the process areas that cause an environmental burden. In the case of the energy footprint of this biorefinery, it is interesting to acknowledge subsystem 5, which is the cogeneration unit that

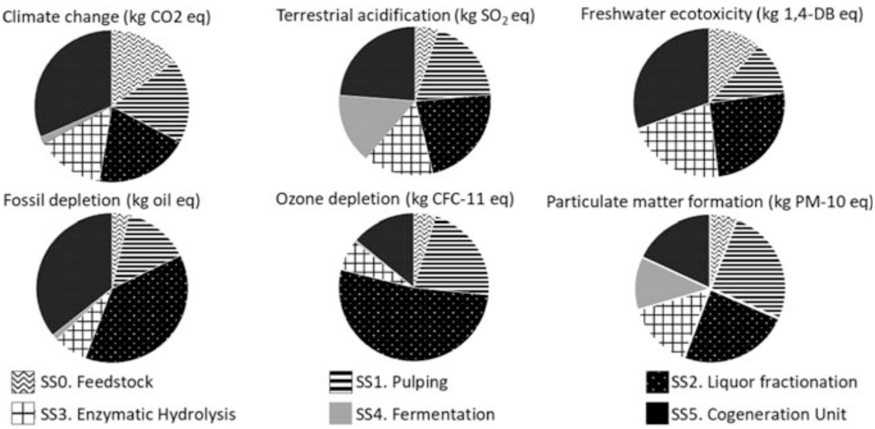

Fig. 6 Life cycle assessment results for six relevant impact categories depicting contributions originated on the process energy requirements in contrast with other processes in the biorefinery

provides energy in the form of electricity and steam to the entire production plant. The results for the six selected impact categories are presented in Fig. 6.

The results presented in Fig. 6 show that for most of the selected impact categories, the CHP unit in the biorefinery was responsible for a very representative percentage of the total impacts. Subsystem 5 contributed significantly to fossil resource depletion (36%), climate change (32%), land acidification (24%) and freshwater ecotoxicity (31%). The relevant contribution of SS5 to fossil depletion is due to the required input of natural gas to meet the energy demands of the process. On the other hand, SS5 is characterized by the handling of process residues to be burnt; therefore, it is important to highlight the importance of CO_2 emissions to air from this subsystem, which mainly contribute to the climate change category.

The energy consumption profile of the biorefinery can be described by two concepts: the impacts of SS5 due to the supply of energy and the energy required from the cogeneration unit. Firstly, the impacts associated with SS5 are the environmental impacts caused by the production of the energy required (Fig. 6). It includes, as mentioned above, the impacts of activities performed in subsystem 5, such as emissions from combustion and the use of natural gas. The overall impacts in SS5 account for, indirectly, all the subsystems in the biorefinery that consume energy. However, the determination of the overall contributions from SS5 does not provide an approximate idea of which areas of the plant represent the greater burdens on the energy footprint of the biorefinery. To determine the subsystems that are more burdening from an energetic point of view, Table 5 shows the energy consumption values of each process.

It can be clearly stated that that the most energy-intensive section of the process in an LCB is the pretreatment. This result agrees with the acknowledgment that other studies have performed on the economic relevance of the lignocellulosic biomass pretreatment, as viewed in Sect. 1.1.2.1. The energy consumption profile

Table 5 Electricity consumptions of the biorefinery for the exploitation of 1 t/h of woodchips Adapted from Kautto et al. (2013), González et al. (2014) and (Dunn et al. 2012)

Process section	Electricity consumption (kW)
Machinery use and chipping	3.6
Feed handling	30.0
Pretreatment	108.0
Cooking	30.0
Pulp washing	18.0
Reject screening	39.6
Pumps	9.6
Agitators	3.6
Compressors, screws, conveyors	7.2
Hydrolysis, fermentation and ethanol recovery	28.8
Pumps	6.0
Agitators	14.4
Compressors, screws, conveyors, mixers	7.2
Molecular sieves	1.2
Storage	0.1
Boiler and turbogenerator	19.2
Utilities	62.4
Cooling water pump and tower system	32.4
Chilled water system	22.8
Instrument air	2.4
Process water	1.2
Sterile water and CIP/CIS systems	3.6
Wastewater treatment	88.8
Enzyme production	1.3
Total energy consumption	342.2

of a biorefinery exploiting lignocellulosic biomass is defined in the pretreatment stage. In contrast to crop-based feedstock biorefineries, LCB pretreatment methods are based on more complex and energy-intensive processes to efficiently breakdown the feedstock and ensure efficient enzymatic hydrolysis (Tran et al. 2013; Zhu and Pan 2010).

4.2.1 Net Energy Gain

Many studies have defined and evaluated the net energy gain (NEG), also known as net energy value (NEV) in the production of biomass-based bioenergy (Arodudu et al. 2017; Illukpitiya et al. 2017; Luo et al. 2009). The NEG is a parameter that characterizes the net energy of a process producing biofuels such as bioethanol. This parameter can be obtained by subtracting the energy input (in the form of direct energy inputs from forestry and harvesting operations, processing and purification) from the energy output, in this case considered as the calorific value of ethanol. The NEG can be viewed as an effectiveness parameter to describe the biomass-to-fuel conversion process; it is a parameter that allows to compare different biorefineries producing ethanol. It can be considered as basis for the evaluation and achievement, for instance, of European targets for increasing energy from renewable sources (Arodudu et al. 2017). In fact, the production of energy from biomass resources can be considered sustainable when the net energy value is positive, therefore, when there is an accountable energy output (Zhu and Zhuang 2012).

As for this case study, there is an energy surplus considering the production of bioethanol, obtaining a positive NEG. Considering the lower heating value of ethanol as 26.8 MJ/kg, and the ethanol production per functional unit (Kautto et al. 2013), the total energy that can be released from ethanol is 1.76 MW per functional unit. Taking the total energy demand of the system under study per functional unit, as presented in Table 5, the estimated NEG for this process results in 17.1 MJ l^{-1}. The energy contained in biomass (beech wood) was not included as an input energy value in the calculation, only direct energy inputs were considered.

Different studies have presented the NEG parameter as a function of the input and output energy values. For instance, Illukpitiya et al. (2017) have determined the NEG for ethanol production from perennial grasses such as switchgrass, eastern gammagrass, big bluestem and indiangrass; on a volume basis, the calculated average net energy gain was 7.9, 5.8, 1.9 and 2.8 MJ·l^{-1} for each feedstock respectively. Farrell et al. (2006) assessed the bioethanol production from corn, and determined a net energy value in the range of 4–9 MJ l^{-1}. Schmer et al. (2008) have obtained a higher NEG value, with an average of 21.5 MJ l^{-1} for the production of cellulosic ethanol from switchgrass.

As can be seen, the NEG parameter presented positive values for different biorefinery systems; conclusively, it can be stated that the use of biomass for sustainable energy production presents positive results. Furthermore, it may be argued that grass species, lignocellulosic feedstock and energy crops show a high probability of resulting in positive NEG values (Illukpitiya et al. 2017).

4.3 Mapping the Environmental Impact of Electricity Consumption for Biorefineries

When analyzing the subject of biorefining under the approach of life cycle assessment, it can be observed that in many occasions, it is common practice to consider that most or part of the energy (in the form of electricity and heat) needed for the processes carried out in the facility is provided by a cogeneration unit available within the production scheme.

While this can mostly be realistic and common practice in many industrial clusters, there is a variable that is left out of the life cycle assessment scheme if energy is considered to be produced in a somewhat sustainable way within processing boundaries. This would be the potential need to use electricity from the grid rather than from a boiler or any similar cogeneration disposition.

On the other hand, it is usual to be generally familiar with the carbon footprint concept. Carbon footprint has been defined as an indicator of the overall balance of greenhouse gas emissions in a system expressed as CO_2 equivalent and based on a life cycle assessment approach (ISO 14067 2012). In the same lines, assessing the energy footprint of biorefineries may imply an evaluation of the energy consumed and or released to obtain a product or a service. However, in terms of energy, there is much more to energy footprint than energy consumption or production. In fact, one of the most relevant factors of energy production or consumption in terms of environmental sustainability is the origin of such energy. The use of fossil derived energy provides a non-sustainable source of electricity and heat for a process. However, if the electricity used in a process has been originated through renewable sources, its environmental burdens will most probably change notoriously.

Combining the fact that biorefineries may not be self-reliable energetically with the importance of energy provenance in energy footprint matters, the most natural step would be to evaluate how the electricity mix from the grid would affect sustainability when evaluated by means of LCA.

A hypothetical evaluation has been considered parting from the case study in Sect. 4.1. The system boundaries of the biorefinery case study considered the production of energy requirements through of subsystem 5. For the purpose of analyzing the impacts related to the source of energy, a sensitivity analysis was performed by means of eliminating subsystem 5 from the system boundaries of the biorefinery. Instead, it was considered that the electricity requirements for each subsystem were fulfilled through the use of electricity from the grid. Furthermore, it is known that the electricity mix in the grid is variant depending on the main energy generation methods of each country. Four countries with different electric mixes were considered for the present sensitivity study, in hopes of analyzing the environmental repercussions of the situational variable of a biorefining facility.

Spain, Turkey, Poland and Finland were the countries evaluated by means of the selection of their respective electricity mix process from the Ecoinvent v3.2 database. The comparative life cycle assessment results are presented in Fig. 7.

As it can be observed in Fig. 7, the differences in the hypothetical geographic location of a biorefinery are clearly influencing the overall environmental results of the impact assessment. Thus, the variation on the electricity country mix attending to location introduces the implications of the origin of energy production to the environmental results. Overall, Poland presents the worse environmental results in four of the evaluated impact categories (climate change, terrestrial acidification, freshwater ecotoxicity and fossil depletion). On the contrary, Finland presents the lowest environmental burdens in all the impact categories considered.

The electricity country mix in Turkey for the year 2015 was characterized by the predominance of natural gas and coal sources with 37.8 and 28.4% shares

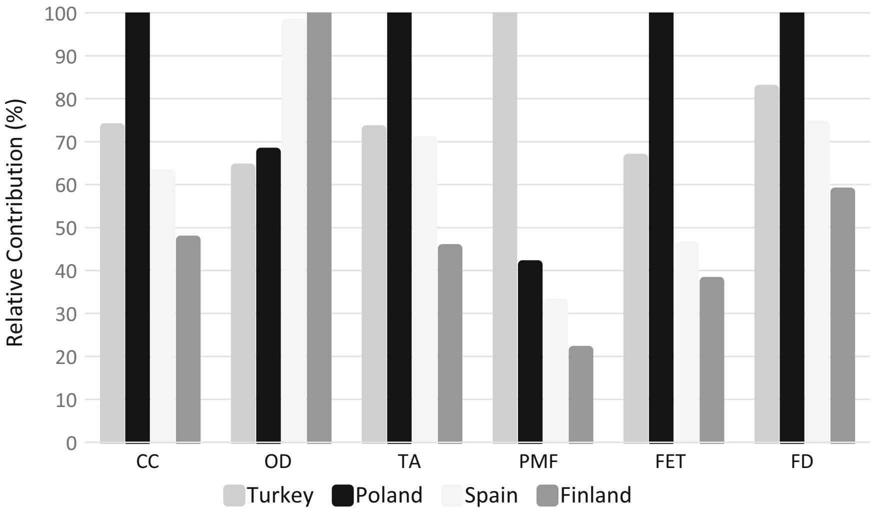

Fig. 7 Comparative analysis of the environmental profile of the biorefinery analyzing different electricity country mix from Turkey, Poland, Spain and Finland

respectively. Hydroelectric energy was produced in a percentage of 25.8%, while wind power represented 4.4% of the overall electricity produced in the country. Other electricity generation methods partake with lower percent values, such as geothermic energy with 1.3%, fuel, diesel and naphtha with a share of 1.6% and, finally, biogas with 0.6% (Ministry of Energy and Natural Resources. Republic of Turkey 2015).

For Poland, available data on the sources that participate in the overall electric mix is that of the year 2015. Coal and lignite power plants represented 71.6% contribution to the global electricity mix. Industrial power plants and gas fired utility power plants, on the other hand, took lower shares, with values of 6.2 and 3.2% respectively. Hydroelectric energy accounted for 5.9%, while wind and other renewable sources represented only 13.2% (Polskie Sieci Elektroenergetyczne (PSE) 2015).

In Spain, for the year 2017, 21.5% of the electricity demand was covered by nuclear power. Electricity produced through coal represented a share of 17%. Combined cycle power plants produced electricity with a contribution of 13.9%. Cogeneration plants represented 11% share. Electricity produced through the use of residual fractions (such as biogas) produced electricity with 1.2% shares. Regarding renewable sources, wind power represented 18.2%, hydroelectric power 7%, solar energy 5.2% and other renewable sources the remaining 1.4% of shares. Electricity imports for Spain represented 3.6% of overall contributions (Red Eléctrica de España 2017).

Finally, the profile of the electric mix in Finland for the year 2017 was composed by 25.2% of nuclear power, 23.9% imports, 12.8% biomass, 17.1% hydroelectric power. Other contributors to the electricity production in the country were natural gas (3.8%), coal (7.2%), oil (0.2%), wind power (5.6%), waste fuels (1.1%) and peat (3.1%) (Finnish Energy 2017). A summary table of the electricity supply contributions by source for each country is represented in Table 6.

As it can be observed through the data depicted in Table 6 as well as the environmental results presented in Fig. 7, the environmental impacts of a facility utilizing electricity from the grid are directly related with the percent contribution of fossil fuels and non-renewable sources to the production of the electricity in the mix. Countries like Turkey or Poland with higher contributions from coal and natural gas sources are clearly more impacted in environmental categories such as climate change (CC) or particulate matter formation (PMF). Contrarily to the tendency of CC, TA, PMF, FET and FD, ozone depletion (OD) depicts an inverse trend in which environmental impacts are higher for Finland and Spain and lower for Poland and Turkey. This is due to the significant contribution to electricity from nuclear power sources. Nuclear power is a carbon free energy source, however it uses uranium and therefore produces radioactive residues, as well as the emission of chlorofluorocarbons (CFCs), which are one of the most ozone depleting substances (Stamford and Azapagic 2011). The decarbonization of the electricity supply system would influence positively the environmental results of a facility. This will be beneficial towards energy security goals. From the results of the comparative evaluation (Fig. 7), it can be observed that the countries with higher percentage of renewable sources (wind power, solar energy, geothermic energy) have less environmentally burdening electricity mixes.

Table 6 Electricity supply contributions by source for Turkey, Poland, Spain and Finland in percent contributions (%)

Electricity source	Turkey[b]	Poland[b]	Spain[a]	Finland[a]
Coal	28.4	71.5	17	10.3
Natural gas	37.9	3.2	–	3.8
Fuel, diesel, naphtha, oil	1.6	–	–	0.2
Hydroelectric	25.8	5.9	7.0	17.1
Wind	4.4	–	18.2	5.6
Solar	–	–	5.2	–
Geothermic	1.3	–	–	–
Residues (Biogas, waste fuels…)	0.6	–	1.2	1.1
Nuclear	–	–	21.5	25.2
Industrial power plants	–	6.2	–	–
Combined cycle power plants	–	–	13.9	–
Cogeneration plants	–	–	11.0	–
Imports	–	–	3.6	23.9
Other renewable sources	–	13.2	1.4	12.8

[a]Data for the year 2017
[b]Data for the year 2015

5 Energy Footprint of Crude Oil Refineries

Biorefineries are developed under the assumption that they will lead to a comparably lower environmental footprint than oil refineries. The main idea on the production of sustainable chemicals lies on the basis that these facilities should environmentally outperform their petrochemical counterparts.

To the best of our knowledge, there are not many studies that directly compare the environmental impacts of the production processes in refineries and biorefineries. The overall sustainability advantages of biorefineries over oil refineries would hypothetically include reducing waste and emissions or increasing energy security by decreasing dependence on imported oil. However, crude oil refineries work with technology that has been developed for many years now and is implemented efficiently. The conclusion is that refineries and biorefineries are two very different systems, with different technologies, in very different situations and development levels that may not be comparable.

When considering a well to wheel environmental analysis, one of the main descriptors being evaluated is exhaust emissions from vehicles using the fuel produced, rather than exclusively considering the production process. It has been determined that vehicles using biodiesel (or other biofuels) produce less SO_2 and CO_2 emissions into the environment than conventional fuel (Bozbas 2008).

Energy for on-site use in oil refineries is generally derived entirely from fossil resources, in fact, from the actual crude oil feedstock. Therefore, it can be said that the consumption and production of energy in a refinery is directly related to the energy footprint of that facility, since fossil fuel is used both to produce energy and to be valorized in chemicals or products. Conventional refineries tend to have high energy efficiencies that result in positive net energy values, deriving in an export of electricity to the grid. The difference with biorefineries is the origin of the energy produced. Refineries produce 100% fossil-based energy, while the percentage of fossil origin in biorefineries tends to be reduced to a minimum. For instance, in the case study evaluated in Sect. 3, the contribution of natural gas to the boiler represents 3% of total contributions. Among different fuels produced in a refinery, energy use has been proven to be higher for gasoline, followed by diesel, LPG and naphtha. The same trend is followed by greenhouse gas emissions obtained from a well to pump (fueling station) perspective (Wang et al. 2004).

In refinery facilities, generally more than half of primary energy is used directly in the process, while the other half is distributed between steam generation and electricity generation. The energy footprint model for petroleum refining shows that energy use (electricity and steam) in manufacturing processes is largely dedicated to heating systems such as furnaces, reboilers or equipment using utility steam, followed by motor-driven units (pumps, fans, compressors). Process cooling and refrigeration as well as other energy-intensive activities represent lower shares. It has been demonstrated that, in general, the petrochemical sector is the largest consumer of fossil fuels among the manufacturing processes (Brueske et al. 2012).

6 Eco-efficiency and Energy Footprint in Biorefineries

Eco-efficiency has been proposed as an environmental management indicator to evaluate both the environmental impact and economic profitability of a process or a product (ISO 14045 2012). Some eco-efficiency indicators have been developed to report measurable quantitative values of sustainability in biorefineries. The relevance of the overall energy footprint of biorefinery facilities can be reflected in energy-related eco-efficiency indicators related to total biorefinery energy consumption, total energy consumption, non-renewable energy consumption or renewable energy consumption rate. They represent the energy consumed in the biorefinery allocated to the total benefit obtained from the products (Chua and Steinmüller 2010).

One of the main products that can be obtained from a biorefinery is electricity (as excess production). The assessment of eco-efficiency can therefore be made by assessing the economic benefit of selling electricity to the grid in relation to the environmental burden of its production. Silalertrusksa et al. (2015) have determined the eco-efficiency indicator defined as US$/kg CO_2 eq. for sugar cane refining products. The results showed that electricity was the most sustainable product, with the highest eco-efficiency values in all scenarios assessed.

The simultaneous consideration of environmental, energy and process parameters, together with the cost-effectiveness of the process in the design of a biorefinery is not easy. Usually, when applying fundamental concepts of life cycle assessment to processes or products, the procedure consists of proposing a series of recommendations for improving environmental parameters after having attained some results. An interesting perspective to guarantee eco-efficiency is the integration of Multi-Objective Optimization (MOO) in life cycle assessment; the result is a method that minimizes environmental impacts, considering specific constrains and objectives. A particular application to the present study would be to provide process alternatives for the optimization of eco-efficiency (environmental and economic factors) in biorefineries, providing, for example, sustainable alternatives for minimizing energy footprint (Mele et al. 2011; Vadenbo et al. 2017).

7 Energy Integration in Biorefineries

In describing the energy footprint of biorefineries, there is little published data on the energy consumption or energy efficiency of industrially implemented systems or real pilot scenarios. It is clear, when comparing the exploitation of crude oil and biomass valorizing methods, that the former is a mature process that has been improved over the last 100 years, while the latter is usually based on processes that still face numerous challenges. One of these challenges is the need for energy optimization.

Process optimization consists of implementing the minimum use of utilities, which would in fact result in minimal water and energy consumption. Optimization of the energy flows in the process implies the interconnection of these flows. This entails the utilization of residual heat in specific flows to provide heating power when necessary. For the optimal implementation of energy optimization methods, system connections should be kept to a minimum. Efficient optimization of energy consumption has the potential to increase the eco-efficiency of systems, for example, by extending the production catalogue without increasing energy input (Rafione et al. 2012).

It is clear that energetic integration has positive effects on reducing the environmental impacts of biorefineries by means of minimizing hot utility use and maximizing heat recovery (Celebi et al. 2017). However, energy integration may not only be achieved through the introduction of efficient interconnections within the same facility, but also through the establishment of global relationships at the industrial clusters. Research shows that the combination of supply systems from different plants in an industrial area presents significant opportunities to improve overall energy efficiency. Integration within industrial parks also makes renewable biomass exploitation opportunities accessible in existing units. Finding a market niche for biomass exploitation at the scale of oil refineries may be feasible as a result of integration into the current industry. The implications of such conclusions are directly related to the immediate possibility of reducing the ecological footprint (Hackl and Harvey 2013). A recognizable example is the implementation of the biorefinery concept for bioenergy production in the pulp and paper industry for an integrated approach (Bajpai 2013).

Beyond exclusive energy integration, some studies approach the feasibility of introducing on-site manufacturing of raw materials that have a major economic and environmental impact due to their production and transport. An example in an LCB is the integration of the enzyme production process necessary for enzymatic hydrolysis within the plant facilities. Enzyme production on-site indirectly decreases energy derived environmental impacts. Some studies suggest the possibility of avoiding enzyme concentration and purification operations after fermentation by means of using the whole culture broth and implementing simultaneous saccharification and fermentation (Olofsson et al. 2017).

8 Conclusions and Future Perspectives

Footprint studies aim to provide common ground on viable options for more sustainable development. In this case, the study of biorefining processes and their energy footprint makes it possible to establish a reference point to determine opportunities for future optimization and sustainable development.

To the best possible extent this chapter has aimed to analyze the biorefinery concept under the energy footprint approach. The objective was to present an overview of the most fundamental aspects of biomass exploitation under the life-cycle assessment approach. The energy footprint of biorefinery systems has been described by means of a bibliographic review that aims to cover the most recent developments, as well as by means of a case study, to specifically define relevant aspects on the energy footprint of biorefineries, such as net energy gain.

The results of this study show that the implementation of biorefineries in industry is a very reliable opportunity as a step towards meeting the sustainability and environmental objectives set out in European policies. The exploitation of biomass has a very favorable potential to replace or support the petrochemical industry. However, biorefineries have the capacity to become increasingly efficient through the implementation of optimization and energy integration methods. The energy footprint of biorefineries has a great capacity to be reduced to a minimum by applying the revised concepts. Future research should be geared towards the environmental study of the implications that energy integration matters can have. If fossil energy fuel in biorefineries is minimized, environmental burdens will tend to be diminished. However, it has been made clear that further comparative analysis among case studies contemplating optimization matters will provide key information on the steps to take regarding environmental sustainability of biorefineries.

Acknowledgements This research was supported by the Spanish Government (Ministry of Economy and Competitiveness) through the ERA-IB2 project 2G-Enzymes (PCIN-2015-031) and the European project STARProBio (Grant Agreement Number 727740). The authors belong to the Galician Competitive Research Group GRC ED431C 2017/29 and to the CRETUS Strategic Partnership (AGRUP2015/02). All these programmes are co-funded by FEDER (EU).

References

Adom FK, Dunn JB (2017) Life cycle analysis of corn-stover-derived polymer-grade l-lactic acid and ethyl lactate: greenhouse gas emissions and fossil energy consumption. Biofuels Bioprod Biorefin 11:258–268. https://doi.org/10.1002/bbb

Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresour Technol 101:4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093

Arodudu OT, Helming K, Voinov A, Wiggering H (2017) Integrating agronomic factors into energy efficiency assessment of agro-bioenergy production—a case study of ethanol and biogas production from maize feedstock. Appl Energy 198:426–439. https://doi.org/10.1016/j.apenergy.2017.02.017

Aziz S, Sarkanen K (1989) Organosolv pulping—a review. Tappi J 72:169–175

Bajpai P (2013) Chapter 2—Biorefinery opportunities in the pulp and paper industry*. Biorefinery Pulp Pap Ind 11–15. https://doi.org/http://dx.doi.org/10.1016/B978-0-12-409508-3.00002-X

Barlow J, Sims RC, Quinn JC (2016) Techno-economic and life-cycle assessment of an attached growth algal biorefinery. Bioresour Technol 220:360–368. https://doi.org/10.1016/j.biortech.2016.08.091

Bioenarea (2010) Definition of the methods for the obtaining of active principles. Bioref

Biorefinery Euroview (2008) Workshop BioreFuture 2008 12/02/08 www.biorefinery-euroview.eu

Biorefinery Euroview, Biopol (2009) Joint deliverable report Biorefinery Euroview (addenda D1 . 2 and D1 . 3) & Biopol (D4 . 2) Note with results indentification, classification and mapping of existing EU biorefineries

Boisen A, Christensen TB, Fu W, Gorbanev YY, Hansen TS, Jensen JS, Klitgaard SK, Pedersen S, Riisager A, Ståhlberg T, Woodley JM (2009) Process integration for the conversion of glucose to 2,5-furandicarboxylic acid. Chem Eng Res Des 87:1318–1327

Bozbas K (2008) Biodiesel as an alternative motor fuel: production and policies in the European Union. Renew Sustain Energy Rev 12:542–552. https://doi.org/10.1016/j.rser.2005.06.001

Brueske S, Sabouni R, Zach C, Andres H (2012) U.S. Manufacturing energy use and greenhouse gas emissions analysis

Budzinski M, Nitzsche R (2016) Comparative economic and environmental assessment of four beech wood based biorefinery concepts. Bioresour Technol 216:613–621

Cassman K, Liska A (2007) Food and fuel for all: realistic or foolish? Biofuels Bioprod Biorefin 1:18–23. https://doi.org/10.1002/bbb

Celebi AD, Ensinas AV, Sharma S, Maréchal F (2017) Early-stage decision making approach for the selection of optimally integrated biorefinery processes. Energy 137:908–916. https://doi.org/10.1016/j.energy.2017.03.080

Chua CBH, Steinmüller H (2010) Development of eco-efficiency indicators for a biorefinery

Chum HL, Johnson DK, Black S, Baker J, Grohmann K, Sarkanen KV (1988) Organosolv pretreatment for enzymatic\rHydrolysis of poplars: I. Enzyme\rHydrolysis of cellulosic residues. Biotechnol Bioeng 31:643–649

Collet P, Lardon L, Hélias A, Bricout S, Lombaert-Valot I, Perrier B, Lépine O, Steyer JP, Bernard O (2014) Biodiesel from microalgae—life cycle assessment and recommendations for potential improvements. Renew Energy 71:525–533. https://doi.org/10.1016/j.renene.2014.06.009

Demirbas A (2010) Biorefineries: for biomass upgrading facilities. Green Energy Technol 26. https://doi.org/10.1007/978-1-84882-721-9

Dunn JB, Mueller S, Wang M, Han J (2012) Energy consumption and greenhouse gas emissions from enzyme and yeast manufacture for corn and cellulosic ethanol production. Biotechnol Lett 34:2259–2263

E4tech, RE-CORD, WUR (2015) From the sugar platform to biofuels and biochemicals. Final report for the European Commission, contract No. ENER/C2/423-2012/SI2.673791. https://doi.org/contract No. ENER/C2/423-2012/SI2.673791

Eaglesham A, Brown W, Hardy R (2000) The biobased economy of the twenty-first century: agriculture expanding into health, energy, chemicals, and materials. World, New York

Elvnert J (2009) Star-COLIBRI: strategic targets for 2020- collaboration initiative on biorefineries

Escamilla-Alvarado C, Poggi-Varaldo HM, Ponce-Noyola MT (2017) Bioenergy and bioproducts from municipal organic waste as alternative to landfilling: a comparative life cycle assessment with prospective application to Mexico. Environ Sci Pollut Res 24:25602–25617. https://doi.org/10.1007/s11356-016-6939-z

European Commission (2010) Energy 2020. A strategy for competitive, sustainable and secure energy. https://doi.org/COM(2010) 639

European Commission (2018) 2020 climate and energy package [WWW Document]. URL https://ec.europa.eu/clima/policies/strategies/2020_en. Accessed 15 Jan 18

Faraco V (2013) Lignocellulose conversion. Enzym Microbial Tools Bioethanol Prod. https://doi.org/10.1007/978-3-642-37861-4

Farrell AE, Plevin RJ, Turner BT, Jones AD, O'Hare M, Kammen DM (2006) Ethanol can contribute to energy and environmental goals. Science (80) 311:506–509

Farzad S, Mandegari MA, Guo M, Haigh KF, Shah N, Görgens JF (2017) Multi-product biorefineries from lignocelluloses: a pathway to revitalisation of the sugar industry? Biotechnol. Biofuels 10:1–24. https://doi.org/10.1186/s13068-017-0761-9

Finnish Energy (2017) Energy Year 2017. Electricity [WWW Document]. URL https://energia.fi/en

Fiorentino G, Ripa M, Mellino S, Fahd S, Ulgiati S (2014) Life cycle assessment of Brassica carinata biomass conversion to bioenergy and platform chemicals. J Clean Prod 66:174–187. https://doi.org/10.1016/j.jclepro.2013.11.043

Gavrilescu M (2014) Biorefinery systems: an overview. In: Bioenergy research: advances and applications, pp 219–241
Giwa A (2017) Comparative cradle-to-grave life cycle assessment of biogas production from marine algae and cattle manure biorefineries. Bioresour Technol 244:1470–1479. https://doi.org/10.1016/j.biortech.2017.05.143
Gnansounou E, Kenthorai Raman J (2016) Life cycle assessment of algae biodiesel and its co-products. Appl Energy 161:300–308. https://doi.org/10.1016/j.apenergy.2015.10.043
Gnansounou E, Pandey A (2017) Life-cycle assessment of biorefineries. Life-Cycle Assess Biorefin. https://doi.org/10.1016/B978-0-444-63585-3.00004-8
Goedkoop M, Heijungs R, Huijbregts M, De Schryver A, Struijs J, Zelm Van R (2009) ReCiPe 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level. University of Leiden, Radboud University Nijmegen, RIVM, Bilthoven, Amersfoort, Netherlands
Gontia P, Janssen M (2016) Life cycle assessment of bio-based sodium polyacrylate production from pulp mill side streams: case study of thermo-mechanical and sulfite pulp mills. J Clean Prod 131:475–484. https://doi.org/10.1016/j.jclepro.2016.04.155
González-García S, Hospido A, Agnemo R, Svensson P, Selling E, Moreira MT, Feijoo G (2011) Environmental life cycle assessment of a Swedish dissolving pulp mill integrated biorefinery. J Ind Ecol 15:568–583. https://doi.org/10.1111/j.1530-9290.2011.00354.x
González-García S, Bonnesoeur V, Pizzi A, Feijoo G, Moreira MT (2014) Comparing environmental impacts of different forest management scenarios for maritime pine biomass production in France. J Clean Prod 64:356–367
González-García S, Gullón B, Rivas S, Feijoo G, Moreira MT (2016) Environmental performance of biomass refining into high-added value compounds. J Clean Prod 120:170–180
Hackl R, Harvey S (2013) Framework methodology for increased energy efficiency and renewable feedstock integration in industrial clusters. Appl Energy 112:1500–1509. https://doi.org/10.1016/j.apenergy.2013.03.083
Haddadi MH, Aiyelabegan HT, Negahdari B (2017) Advanced biotechnology in biorefinery: a new insight into municipal waste management to the production of high-value products. Int J Environ Sci Technol https://doi.org/10.1007/s13762-017-1424-x
Harmsen P, Huijgen W, López L, Bakker R (2010) Literature review of physical and chemical pretreatment processes for lignocellulosic biomass. Food Biobased Res, 1–49
Harris ZM, Spake R, Taylor G (2015) Land use change to bioenergy: a meta-analysis of soil carbon and GHG emissions. Biomass Bioenerg 82:27–39. https://doi.org/10.1016/j.biombioe.2015.05.008
Hatti-Kaul R (2010) Biorefineries- a path to sustainability? Crop Sci 50, S-152-S-156. https://doi.org/10.2135/cropsci2009.10.0563
Heinzle E, Biwer AP, Cooney CL (2006) Development of sustainable bioprocesses: modelling and assessment
Hernández V, Romero-García JM, Dávila JA, Castro E, Cardona CA (2014) Techno-economic and environmental assessment of an olive stone based biorefinery. Resour Conserv Recycl 92:145–150. https://doi.org/10.1016/j.resconrec.2014.09.008
Himmel ME, Ding S-Y, Johnson DK, Adney WS, Nimlos MR, Brady JW, Foust TD (2007) Biomass recalcitrance: engineering plants and enzymes for biofuels production. Science (80) 315:804–807. https://doi.org/10.1126/science.1137016
IEA Bioenergy (2018) Global database of biomass conversion facilities, including advanced biofuels, combustion, gasification and pyrolysis plants [WWW Document]. URL http://www.ieabioenergy.com/installations/
Illukpitiya P, Reddy KC, Bansal A (2017) Modeling net energy balance of ethanol production from native warm season grasses. Energy Econ 64:346–352. https://doi.org/10.1016/j.eneco.2017.04.008
ISO 14044 (2006a) ISO 14044: Life cycle assessment—requirements and guidelines. Int Organ Stand https://doi.org/10.1136/bmj.332.7550.1107

ISO14044 (2006b) ISO 14044, Environmental management—life cycle assessment—Requirements and guidelines 2006, 54
ISO 14045 (2012) ISO 14045:2012—Environmental management—eco-efficiency assessment of product systems–Principles, requirements and guidelines, 2012
ISO 14067 (2012) Carbon footprint of products—requirements and guidelines for quantification and communication
ISO14040 (2006) ISO 14040-Environmental management—life cycle assessment—principles and framework, ISO 14040. https://doi.org/10.1016/j.ecolind.2011.01.007
Kamm B, Kamm M (2004) Principles of biorefineries. Appl Microbiol Biotechnol 64:137–145. https://doi.org/10.1007/s00253-003-1537-7
Kamm B, Gruber PR (2006) Handbook of fuels beyond oil and gas : the methanol economy Bailey's industrial oil and fat products oil refineries in the 21st Century, biorefineries—industrial processes and products
Kamm B, Gruber PR, Kamm M (2008) Biorefineries-industrial processes and products: status quo and future directions, biorefineries-industrial processes and products: status quo and future directions. https://doi.org/10.1002/9783527619849
Kamm B, Gruber PR, Michael K (2016) Biorefineries—industrial processes and products. Ullmann's Encycl Ind Chem 1–38. https://doi.org/10.1002/14356007.l04_l01.pub2
Kautto J, Realff MJ, Ragauskas AJ (2013) Design and simulation of an organosolv process for bioethanol production. Biomass Convers Biorefin 3:199–212. https://doi.org/10.1007/s13399-013-0074-6
Khoshnevisan B, Rafiee S, Tabatabaei M, Ghanavati H, Mohtasebi SS, Rahimi V, Shafiei M, Angelidaki I, Karimi K (2017) Life cycle assessment of castor-based biorefinery: a well to wheel LCA. Int J Life Cycle Assess 1–18. https://doi.org/10.1007/s11367-017-1383-y
Kim S, Dale BE (2015) Comparing alternative cellulosic biomass biorefining systems: centralized versus distributed processing systems. Biomass Bioenerg 74:135–147. https://doi.org/10.1016/j.biombioe.2015.01.018
King D (2010) The future of industrial biorefineries. World Econ Forum Rep 1:1–38. https://doi.org/10.1086/294443
Kleinert M, Barth T (2008) Phenols from lignin. Chem Eng Technol 31:736–745. https://doi.org/10.1002/ceat.200800073
Laure S, Leschinsky M, Fröhling M, Schultmann F, Unkelbach G (2014) Assessment of an Organosolv lignocellulose biorefinery concept based on a material flow analysis of a pilot plant. Cellul Chem Technol 48:793–798
Levasseur A, Bahn O, Beloin-Saint-Pierre D, Marinova M, Vaillancourt K (2017) Assessing butanol from integrated forest biorefinery: a combined techno-economic and life cycle approach. Appl Energy 198:440–452. https://doi.org/10.1016/j.apenergy.2017.04.040
Li J, Wang Y, Yan B (2018) The hotspots of life cycle assessment for bioenergy: a review by social network analysis. Sci Total Environ 625:1301–1308. https://doi.org/10.1016/j.scitotenv.2018.01.030
Lin Z, Nikolakis V, Ierapetritou M (2015) Life cycle assessment of biobased p -xylene production. Ind Eng Chem Res 54:2366–2378. https://doi.org/10.1021/ie5037287
Luo L, van der Voet E, Huppes G (2009) An energy analysis of ethanol from cellulosic feedstock-Corn stover. Renew Sustain Energy Rev 13:2003–2011. https://doi.org/10.1016/j.rser.2009.01.016
Mandegari MA, Farzad S, van Rensburg E, Görgens JF (2017) Multi-criteria analysis of a biorefinery for co-production of lactic acid and ethanol from sugarcane lignocellulose. Biofuels Bioprod Biorefin 11:971–990. https://doi.org/10.1002/bbb
Martín M, Grossmann IE (2013) On the systematic synthesis of sustainable biorefineries. Ind Eng Chem Res 52:3044–3064. https://doi.org/10.1021/ie2030213
Mele FD, Kostin AM, Guillén-Gosálbez G, Jiménez L (2011) Multiobjective model for more sustainable fuel supply chains. A case study of the sugar cane industry in Argentina. Ind Eng Chem Res 50:4939–4958. https://doi.org/10.1021/ie101400g

Ministry of Energy and Natural Resources. Republic of Turkey (2015) Electricity mix 2015 [WWW Document]. URL http://www.enerji.gov.tr/en-US/Mainpage

Modahl IS, Brekke A, Valente C (2015) Environmental assessment of chemical products from a Norwegian biorefinery. J Clean Prod 94:247–259. https://doi.org/10.1016/j.jclepro.2015.01.054

Morgan-Sagastume F, Valentino F, Hjort M, Cirne D, Karabegovic L, Gerardin F, Johansson P, Karlsson A, Magnusson P, Alexandersson T, Bengtsson S, Majone M, Werker A (2014) Polyhydroxyalkanoate (PHA) production from sludge and municipal wastewater treatment. Water Sci Technol 69:177–184. https://doi.org/10.2166/wst.2013.643

Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch M (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 96:673–686. https://doi.org/10.1016/j.biortech.2004.06.025

Mosquera-Corral A, Carvalho G, Fra-Vázquez A, Ntaikou I, Oleskowicz-Popiel P, Palmiero-Sánchez T, Reis MAM, Suárez-Ojeda ME (2017) Recovery of organic added value products from wastewater. In: Innovative wastewater treatment & resource recovery technologies: impacts on energy, economy and environment, pp 399–421

Moussa HI, Elkamel A, Young SB (2016) Assessing energy performance of bio-based succinic acid production using LCA. J Clean Prod 139:761–769. https://doi.org/10.1016/j.jclepro.2016.08.104

Nova Institute, Consortium, B.B.I. (2017) Biorefineries in Europe 2017

Ofori-Boateng C, Lee KT (2014) An oil palm-based biorefinery concept for cellulosic ethanol and phytochemicals production: sustainability evaluation using exergetic life cycle assessment. Appl Therm Eng 62:90–104. https://doi.org/10.1016/j.applthermaleng.2013.09.022

Olofsson J, Barta Z, Börjesson P, Wallberg O (2017) Integrating enzyme fermentation in lignocellulosic ethanol production: life-cycle assessment and techno-economic analysis. Biotechnol Biofuels 10:51. https://doi.org/10.1186/s13068-017-0733-0

Pandey MP, Kim CS (2011) Lignin depolymerization and conversion: a review of thermochemical methods. Chem Eng Technol 34:29–41. https://doi.org/10.1002/ceat.201000270

Parajuli R, Knudsen MT, Birkved M, Djomo SN, Corona A, Dalgaard T (2017) Environmental impacts of producing bioethanol and biobased lactic acid from standalone and integrated biorefineries using a consequential and an attributional life cycle assessment approach. Sci Total Environ 598:497–512. https://doi.org/10.1016/j.scitotenv.2017.04.087

Pereira LG, Chagas MF, Dias MOS, Cavalett O, Bonomi A (2015) Life cycle assessment of butanol production in sugarcane biorefineries in Brazil. J Clean Prod 96:557–568. https://doi.org/10.1016/j.jclepro.2014.01.059

Polskie Sieci Elektroenergetyczne (PSE) (2015) Annual report 2015 [WWW Document]. URL https://www.pse.pl/web/pse-eng

Prasad A, Sotenko M, Blenkinsopp T, Coles SR (2016) Life cycle assessment of lignocellulosic biomass pretreatment methods in biofuel production. Int J Life Cycle Assess 21:44–50. https://doi.org/10.1007/s11367-015-0985-5

Rafione T, Marinova M, Montastruc L, Domenech S, Srinivasan B, Paris J (2012) Optimization of water and energy consumption in an integrated forest biorefinery. J Sci Technol For Prod Process 2:54–59

Rahimi V, Karimi K, Shafiei M, Naghavi R, Khoshnevisan B, Ghanavati H, Mohtasebi SS, Rafiee S, Tabatabaei M (2018) Well-to-wheel life cycle assessment of Eruca Sativa-based biorefinery. Renew Energy 117:135–149. https://doi.org/10.1016/j.renene.2017.10.035

Raman JK, Gnansounou E (2015) LCA of bioethanol and furfural production from vetiver. Bioresour Technol 185:202–210. https://doi.org/10.1016/j.biortech.2015.02.096

Red Eléctrica de España (2017) El sistema eléctrico español. Avance 2017 [WWW Document]. URL http://www.ree.es/es

Sarkar N, Ghosh SK, Bannerjee S, Aikat K (2012) Bioethanol production from agricultural wastes: an overview. Renew Energy 37:19–27. https://doi.org/10.1016/j.renene.2011.06.045

Schmer MR, Vogel KP, Mitchell RB, Perrin RK (2008) Net energy of cellulosic ethanol from switchgrass. Proc Natl Acad Sci 105:464–469. https://doi.org/10.1073/pnas.0704767105

Seghetta M, Hou X, Bastianoni S, Bjerre AB, Thomsen M (2016) Life cycle assessment of macroalgal biorefinery for the production of ethanol, proteins and fertilizers—a step towards a regenerative bioeconomy. J Clean Prod 137:1158–1169. https://doi.org/10.1016/j.jclepro.2016.07.195

Silalertruksa T, Gheewala SH, Pongpat P (2015) Sustainability assessment of sugarcane biorefinery and molasses ethanol production in Thailand using eco-efficiency indicator. Appl Energy 160:603–609. https://doi.org/10.1016/j.apenergy.2015.08.087

Souza SP, Gopal AR, Seabra JEA (2015) Life cycle assessment of biofuels from an integrated Brazilian algae-sugarcane biorefinery. Energy 81:373–381. https://doi.org/10.1016/j.energy.2014.12.050

Stamford L, Azapagic A (2011) Sustainability indicators for the assessment of nuclear power. Energy 36:6037–6057. https://doi.org/10.1016/j.energy.2011.08.011

Stuart P, El-Halwagi M (2014) Integrated biorefineries: design, analysis and optimization. https://doi.org/10.1017/CBO9781107415324.004

Tao L, Tan ECD, McCormick R, Zhang M, Aden A, He X, Zigler BT (2014) Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. Biofuels Bioprod Biorefin 8:30–48. https://doi.org/10.1002/bbb

Tomei J, Helliwell R (2016) Food versus fuel? Going beyond biofuels. Land use policy 56:320–326. https://doi.org/10.1016/j.landusepol.2015.11.015

Tran UPN, Van Vu KL, Nguyen QD, Le PTK, Phan TD, Mochidzuki K, Kobayashi S, Seo D-J, Sakoda A (2013) Energy balance of small-scale biorefinery system. Environ Sci 26:489–496. https://doi.org/10.11353/sesj.26.489

Uihlein A, Schebek L (2009) Environmental impacts of a lignocellulose feedstock biorefinery system: an assessment. Biomass Bioenerg 33:793–802. https://doi.org/10.1016/j.biombioe.2008.12.001

Vadenbo C, Tonini D, Astrup TF (2017) Environmental multiobjective optimization of the use of biomass resources for energy. Environ Sci Technol 51:3575–3583. https://doi.org/10.1021/acs.est.6b06480

Vaskan P, Pachón ER, Gnansounou E (2018) Techno-economic and life-cycle assessments of biorefineries based on palm empty fruit bunches in Brazil. J Clean Prod 172:3655–3668. https://doi.org/10.1016/j.jclepro.2017.07.218

Vohra M, Manwar J, Manmode R, Padgilwar S, Patil S (2014) Bioethanol production: feedstock and current technologies. J Environ Chem Eng 2:573–584. https://doi.org/10.1016/j.jece.2013.10.013

Wang M, Lee H, Molburg J (2004) Allocation of energy use in petroleum refineries to petroleum products. Int J Life Cycle Assess 9:34–44. https://doi.org/10.1007/BF02978534

Wernet G, Bauer C, Steubing B, Reinhard J, Moreno-Ruiz E, Weidema B (2016) The ecoinvent database version 3 (part I): overview and methodology. Int J Life Cycle Assess 21:1218–1230. https://doi.org/10.1007/s11367-016-1087-8

Zheng Y, Pan Z, Zhang R (2009) Overview of biomass pretreatment for cellulosic ethanol production. Int J Agric Biol Eng 2:51–68. https://doi.org/10.3965/j.issn.1934-6344.2009.03.051-068

Zhu JY, Pan XJ (2010) Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation. Bioresour Technol 101:4992–5002. https://doi.org/10.1016/j.biortech.2009.11.007

Zhu JY, Zhuang XS (2012) Conceptual net energy output for biofuel production from lignocellulosic biomass through biorefining. Prog Energy Combust Sci 38:583–598. https://doi.org/10.1016/j.pecs.2012.03.007