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Agricultural Waste to Value-Added Products

Technical, Economic and Sustainable Aspects

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Foreword

A must-read book for young and experienced researchers in the field of biomass valorization. The chapters in the book are well designed to educate and inform the readers about the various processes and possibilities available in the domain of biomass conversion. The book has chapters on conversion processes as well as talks about the applications of the different products of biomass conversion. It would be useful to get a holistic understanding of the nuances in biomass utilization and value addition to high-value products. With the increased emphasis on climate change mitigation processes, the book becomes all the more relevant in terms of biomass valorization and application for products.

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Thallada Bhaskar

Preface

Cultivation, harvest, and crop processing result in enormous quantity of agricultural waste generation. The current practice of mass burning or mulching in land leads to air pollution and land pollution. Adopting appropriate management techniques for agricultural waste management is an essential aspect of sustainable development. Alongside, the urge for renewable energy sources is ever increasing following the depletion of fossil reserves globally. Waste to energy processes and biomass to biofuel have begun taking shape in the global energy sector, curbing both the problems of solid waste and energy demand. Waste to value-added products is a sustainable way of managing massive agricultural waste.

This book reviews ongoing research and recent trends in creating value-added products from agricultural waste. It provides an overview of agricultural waste treatment, management, and sustainable use as biofuels, fertilizers, and other value-added products. In addition, techno-economic analysis is used to present an assessment of the economics and practical feasibility of agricultural waste-based end products. This book contains 18 chapters providing state-of-the-art reviews on the current developments and research on agricultural waste production and treatment methodologies. Consequently the book is divided into two sections: Chapters 1–8 focusing on the advancement in technologies involved in the production of value-added products from agricultural waste and Chapters 9–18 focusing on the application of various value-added products like biochar, bio-oil, nano-materials, etc. in the current scenario for various purposes. Chapters 1 and 2 provide detailed information regarding the production of agricultural by-products along with the challenges the agro-industries face due to conventional/traditional technology on the global platform. These chapters showcase the disadvantages of the traditional methods involved in biomass waste treatment and thereby stress upon the need of novel technologies to be implemented. Chapter 3 focuses on the concept of circular bio-economy emphasizing the technoeconomical aspects of advanced technologies for bioenergy production from agricultural waste. Furthermore, it examines the environmental performance of agricultural waste via life cycle assessment of biofuel generation following modern approaches. Chapters 4 and 5 focus on the bioelectrochemical system for agricultural residue treatment and their effects on bioenergy production and other value-added product recovery. In addition, recent developments in potentially impending research areas of BES supporting agricultural waste are also covered to prepare this nascent technology for large-scale deployment. Chapter 6 provides a comprehensive insight into the trends, challenges, and prospects related to microbial methods of transformations of agricultural waste into organic fertilizers and its further sustainable development. Chapters 7 and 8 provide a critical review of the current thermo-chemical conversion technologies to turn “agro-trash into treasure” and details on the recent advancements in thermo-chemical technologies, and the influencing parameters for their practical applications. Chapter 9 deals with distinctive agricultural wastes, their impact on the environment, and the significance of lignocellulosic characteristics for the blossoming of biochar through various thermochemical techniques. Alongside, it also emphasizes on different characterization studies of biochar implicating its efficacy for various applications like adsorption, energy resource, soil improvement, etc. Chapter 10 focuses on providing insights into the properties of agricultural waste-based biochar related to carbon fixation and sequestration using greenhouse gas (mainly CO_2) balance model and energy balance model. Chapter 11 elucidates the contaminant management potential of biochar obtained from different feedstock. On the other hand, Chapter 12 focuses on the review of the valorization of sugarcane bagasse fly ash and its application as an adsorbent for heavy metal removal. The investigation of different feedstock composition, microstructure, by-products, and their applications has been done intensively in Chaps. 13 and 14. Chapters 15 and 16 focus on the mechanisms of synthesizing nano-materials (NMs) from agricultural wastes (AWs) and their possible applications in various industries to reduce the accumulation of various contaminants, via analyzing different synthesis methods. The book closes with Chaps. 17 and 18, which provide detailed information on the large-scale feasibility of different waste-to-energy conversion technologies for both centralized and decentralized systems, alongside their advantages and responsibilities in building a sustainable circular bio-economy.

We believe this book will be an invaluable resource for academics, policymakers, practitioners, and students interested in the field of agricultural waste management.

Khordha, India — Remya Neelancherry
Troy, NY, USA — Bin Gao
São Cristóvão, Brazil — Alberto Wisniewski, Jr

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The editors are grateful to the chapter authors and publishers in bringing this collection of key information relating to conversion of agricultural waste to value-added products into the format of a book. We appreciate the time and effort put in by everyone who contributed to this volume. The views and opinions conveyed in each chapter of this book are those of the respective authors and should not be construed as representing the organizations for which they work.

Despite the great effort that editors have invested in this work and the extensive checks conducted by many experts in the field of valorization of agricultural by-products, mistakes may have been made. We would like to highlight that any comments or suggested changes to improve and update the book contents for future editions are welcomed.

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Bin Gao
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About the Editors

Remya Neelancherry is an Associate Professor at the School of Infrastructure, Indian Institute of Technology Bhubaneswar, Odisha, India. She pursued her PhD in Environmental Engineering at National Chiao Tung University, Taiwan, and MTech in Environmental Engineering from Indian Institute of Technology Madras, India, and RWTH Aachen University, Germany (DAAD scholar). She has expertise in microwave for solid waste management, advanced oxidation process for water and wastewater treatment, and the development of novel nano-catalyst and characterization of catalysts for bio-refractory pollutant removal. She is a member of the American Society of Civil Engineers, American Chemical Society, Indian Water Works Association, Institute of Engineers (India), and a senior Member of Asia-Pacific Chemical, Biological & Environmental Engineering Society. She received the Innovation award in National Green Charcoal Hackathon, India, and Outstanding Women in Engineering Award, Women Researcher Award, and Golden Bamboo Scholarship from National Chiao Tung University, Taiwan, German Academic Exchange Fellowship, European Research Council Mobility Grand, etc. She has several publications in reputed international journals, books, and conference proceedings.

Bin Gao is the Kodak Chair Professor in the Department of Civil and Environmental Engineering at Rensselaer Polytechnic Institute. Prior to this, he was a professor at University of Florida, a research associate at Cornell University, and a postdoctoral research associate at Yale University. He earned his PhD degree at Cornell University and his B.S. and M.S. degrees at Nanjing University. Prof. Gao's research mainly focuses on biochar technology, environmental nanotechnology, and contaminant fate and transport. He has an extensive list of publications in the field of environmental science and engineering. Prof. Gao has received several prestigious awards and professional honors including Highly Cited Researcher, SSSA Fellow, and NSF CAREER Award.

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Introduction: Growth of Agricultural Waste, Its Disposal, and Related Environmental Issues

1

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Kuppusamy Vaithilingam Selvakumar, Selvakumar Periyasamy,
and Abdi Nemera Emana

Abstract

Agricultural wastes are byproducts of growing and processing agricultural raw materials such as vegetables, fruits, livestock, dairy products, poultry, and crops. They consist of the agricultural processing of non-product outputs that may include elements that are valuable to people. Still, the economic value of the material is less than the cost of gathering, processing, transporting, and processing them for those uses. They can exist as solids, liquids, or slurries, and their percentage composition will vary according to the farming system and kind. Agricultural waste includes waste from animals (manure, animal carcasses); waste from the food industry, for instance, 80% of corn is wasted and only 20% is canned; waste from crops (sugarcane bagasse, corn stalks, fruit and vegetable drop and culls, prunings); and toxic and dangerous agricultural waste (herbicides, insecticides, pesticides, etc.). Wastes from the inappropriate use of intensive farming techniques and the improper handling of agricultural chemicals typically accompany agricultural development, negatively impacting rural settings and the global environment. This chapter thoroughly summarizes current developments in the idea and production of agricultural waste. In addition, characteristics of the agricultural waste strategy, hierarchy of agricultural waste, and different

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management techniques such as landfilling, incineration, composting, anaerobic digestion, and other methods, as well as health and environmental concerns, are discussed.

Keywords

Agricultural waste · Agricultural development · Waste disposal · Sustainable resources · Environmental issues

1.1 Introduction

Increased agricultural productivity is required due to the growing human population. Over the previous 50 years, agricultural output is thought to have expanded by a factor of more than 3. Other elements that have boosted agricultural output include advancing green revolution technologies and spreading agriculturally productive soil. Around 24 million tons of food are produced globally by the agriculture sector. A substantial volume of nutrients, water, and energy is extracted from the soil during crop harvest. As a result, the ground becomes sterile and adverse to developing new species and ecosystems. This is especially true of land used for industrial monoculture farms. Food is a necessity that we cannot live without, but it is also clear that agriculture affects the ecosystem. For instance, it is well known that around 21% of greenhouse gas (GHG) emissions are caused by agriculture because of agriculture's negative consequences on marine life, human health, and the environment; a more effective and efficient way of processing agricultural solid wastes is needed to increase agricultural production (Jayakumar et al. 2023; Periyasamy et al. 2023). The agricultural wastes produced by agricultural activities seriously harm the environment and have a worrisome impact on the natural environment's ecological system (Adejumo and Adebiyi 2020; Selvakumar et al. 2022).

Agricultural items such as vegetables, fruits, grains, dairy, meat, poultry, and other unprocessed agricultural products are produced and processed, and as a result, agricultural wastes are produced (Kavitha et al. 2022; Periyasamy et al. 2022). Organic and inorganic waste products produced at a farm from various farming operations, such as dairy farming, horticulture, seed planting, livestock breeding, harvesting, and processing, are examples of agricultural wastes (Selvakumar et al. 2021; Selvakumar and Sivashanmugam 2018). Because they are not the main products, the byproducts of agricultural activities are frequently referred to as "agricultural waste." Because they are readily available, reproducible, and virtually wholly free, agricultural wastes can be important. They are waste products from the processing and manufacturing of agricultural products that may contain components that are advantageous to people but whose economic value is less than the cost of collecting, transporting, and processing them for such reasons. These agricultural waste materials might be solids, liquids, or slurries, depending on the system and type of agricultural techniques used to produce them. Agricultural waste is also referred to as agro-waste. These wastes include both hazardous and toxic agricultural wastes such as herbicides, insecticides, and pesticides, as well as animal waste such as animal carcasses and manure; food processing waste (80% of corn is wasted since only 20% is canned); crop waste such as leftover leaves, stalks, straw, husks, roots, and shells; and waste from the harvesting of crops (Jayakumar et al. 2022; Selvakumar et al. 2019; Kavitha et al. 2021). Estimating agricultural waste is uncommon, although it is generally accepted that they provide a sizable portion of the world's total garbage to the industrialized world. As agricultural production has increased, the amounts of livestock waste, crop residues, and other agricultural byproducts (Obi et al. 2016; Neh 2020) have also increased. Techniques for efficient processing of agricultural wastes needed for eco-friendly agriculture and sustainable growth have recently been attracted to prevent the contamination of air, water, and land resources and the transmission of dangerous compounds.

The waste management hierarchy system (WMHS) must be used since agricultural waste harms the environment. Particularly, waste management lessens the influence of agricultural waste on the ecological system. As a result, waste management includes waste minimization (reduction), recovery, reuse, and recycling, in addition to trash disposal (landfilling). The most advantageous choice from the abovementioned waste management system is waste reduction or minimization, and the least advantageous alternative is disposal (landfilling). Thus, the development of agricultural waste, its disposal, environmental challenges, and agricultural waste management systems are the main topics of this study.

1.2 Concept and Generation of Agricultural Waste

Because of population expansion, which directly impacts the economy and the environment, the waste output is increasing daily (Dhandayuthapani et al. 2022; Mohamed et al. 2022b). Agricultural wastes have recently emerged as a substantial source of pollution. The wastes produced by the agricultural industries include animal dung, residual plant material from harvesting, lipids, proteins, and other organic materials (Mohamed et al. 2022a). A growing government priority is agricultural waste management (AWM) for sustainable development and ecological agriculture. For instance, almost all of these agricultural "wastes" can be easily metabolized. In addition to giving plants vital nutrients, the byproducts of the decomposition process also make the soil porous and enhance its properties, particularly its capacity to hold water, helping to promote healthy, sustainable agriculture.

Moreover, the haphazard burning of wastes like cattle manure and straws in an agricultural nation leads to several environmental issues. The safety of the environment's population health has always been under pressure because of the growing garbage and improper clearance, especially in emerging nations (Selvakumar and Sivashanmugam 2017). At the same time, this has amplified the contribution of these nations to the worldwide emissions of GHGs (Hai and Tuyet 2010; Elbasiouny et al. 2020).

1.2.1 Waste from Farming Activities

Agricultural operations result in the production of waste from farming activities. This waste includes harvest trash, fertilizer runoff from fields, pesticides in water streams, the atmosphere, soils, and manure and other waste products from slaughterhouses, poultry houses, and farms (Asaithambi et al. 2020; Rajesh Banu et al. 2021). A sizable amount of agricultural waste, including animals and manure, has not been immediately disposed of during the development and management of family farms, dangerously damaging the environment. Small farms benefit from the economic and environmental advantages of recycling animal and poultry manure to fertilize crops.

1.2.2 Waste from Livestock

Livestock waste is defined as animal excrement, bedding material, water from rain or other sources, soil, hair, feathers, and other detritus typically handled with animal waste. Excreta (manure), litter like wood shavings or straws, waste feed or bedding materials, dead birds or animals, feathers, broken eggs, and farm sweep-outs are all examples of waste from the livestock and poultry industries. Additionally, it might contaminate water supplies and aid in the spread of infectious diseases. Improper water disposal planning could cause discontent due to the release of smell and infectivity of water sources. The efficient use of waste on large farms requires pollution and the spread of illnesses and infections (Parihar et al. 2019).

Meanwhile, the meat, milk, and egg sectors all produce a lot of wastes that, if not properly managed, could affect the environment. The wastes produced by the cattle industry can significantly complement inorganic fertilizers. Animal manure is a valuable source of nutrients and organic matter that can preserve soil fertility and increase crop yields. According to studies conducted on animals, feces and urine, typically employed as manure, contain between 55% and 90% of the nitrogen and phosphorus content of the animal feed. Recovered chicken and swine manure from confinement feeding facilities have been supplied to beef cattle, dairy cattle, and sheep. It was discovered that these feeds caused no severe health risks to ruminants and poultry nor did they have any detrimental effects on the quality of the meat, eggs, or milk. Biogas has traditionally been produced from animal manure. However, the health of people and animals is greatly endangered by the negligent disposal of livestock waste on farmlands, direct discharge to waterways, and percolation to groundwater, typically in bypass flow via cracks and fissures (Atinkut et al. 2020).

Animal manure storage, field application, and livestock waste are the main sources of offensive odors. For neighbors living near animal manure, odor intensity is frequently intolerable. Since 1850, greenhouse gas methane (GHGM) in the atmosphere has increased by 45% globally. This growth has been strongly influenced by increases in livestock production, with enteric fermentation of ruminants estimated to account for 13–15% of the total 1990s methane emissions and livestock waste for 5%. Animal and human health hazards are often associated with improperly managed livestock manure. As a result, there is a pressing need for a thorough investigation of effective ways to use animal waste to develop environmentally responsible, long-term livestock production systems. Systems must ensure their long-term use as organic manure, alternative feed, and a source of biogas and decrease its detrimental impacts on the environment, the health of people and animals, and both (Yang et al. 2021).

1.2.3 Waste from Processing

Processing waste from agriculture is created when crop or animal products are processed for human consumption in facilities like abattoirs or slaughterhouses. These wastes include banana peels, hoofs, bones, and other objects. Additionally, some processing wastes can be employed as natural antimicrobials. Pomegranate peels, lemon peels, and green walnut husks are a few examples. Environmental risks are associated with organic wastes, but they also hold the potential for creating bio-based products like bioenergy and biofertilizers, as well as delicacies like mushrooms. A portion of the agricultural waste is turned into animal feed. However, these wastes have various components, including many proteins, carbohydrates, and minerals. Including these nutrients in raw materials allows for the development of microorganisms in favorable environments. These bacteria can recycle raw materials through fermentation processes (Sadh et al. 2018). Process residues remain leftovers even after the crop has been processed into another meaningful resource. Agricultural husks, seeds, leaves, straws, stalks, stems, roots, shells, peels, pulp, stubble, bagasse, molasses, and other materials make up these wastes, as represented in Fig. 1.1 and employed in various industries, including manufacturing, soil enhancement, fertilizer application, and animal feeding.

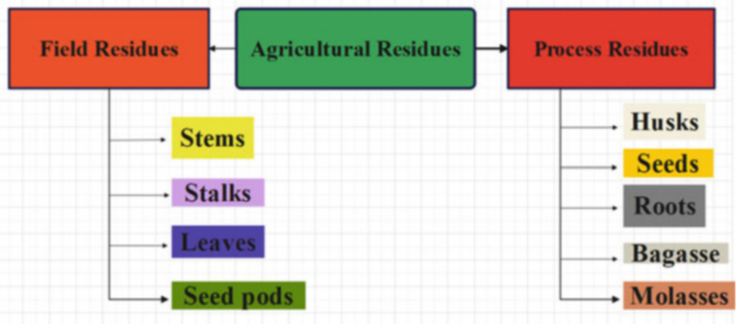

Fig. 1.1 Agricultural wastes and their source classifications

1.3 Characteristics of Agricultural Waste

Due to the abundance of organic components in agricultural and food industry wastes, biological degradation occurs often. These wastes typically have enough phosphorus, trace elements, and nitrogen for biological growth. Depending on the type of procedure, the size and age of the plant, the season, and the waste's composition, both the amount and composition of solid and liquid wastes from farming and food processing might vary. Based on their physical and chemical characteristics, agricultural wastes are categorized. Agricultural wastes' physical characteristics include their weight, volume, total solids, and moisture content, while their chemical characteristics include nitrogen, phosphorus, and potassium levels. The characteristics of agricultural waste are described under the physical characteristics. They indicate the quantity and consistency of the material to be handled by machinery and in treatment and storage facilities.

On the other hand, nitrogen, phosphorus, and potassium are present in the chemical makeup of agricultural waste. The makers, planners, and designers of waste systems value these chemical components highly. The main waste utilization method for agricultural waste is land application. When creating an agricultural waste management strategy, the main factors considered are nitrogen, phosphorus, and potassium.

1.4 Approaches and Hierarchy of Agricultural Waste Management Systems

The term "agricultural waste management system" (AWMS) refers to a structured framework that makes sure all crucial elements are established and managed to watch over and utilize agricultural production's wastes in a way that preserves or improves the sustainability of the environment's plant, animal, and energy resources. AWM has recently captured the interest of policymakers interested in ecological agriculture and sustainable development. The conventional method of handling agricultural waste has traditionally involved discharging it into the environment, whether or not it has been treated. Wastes need to be viewed as valuable resources rather than unwanted and undesirable things to prevent contaminating natural resources, air, water, and land and stop the spread of harmful compounds. This will necessitate the employment of improved agricultural waste management methods, a shift in perspective, more advanced technology, and financial incentives. The quality of soil, water, and air can be significantly harmed by the incorrect management or nontreatment of organic wastes, particularly animal manure. Staggered wastes are a breeding ground for insects and a vector for disease. The unfettered degradation of organic wastes results in noxious fumes and ammonia volatilization, which causes acid rain (Obi et al. 2016).

Methane concentration in the atmosphere has surged during the past 5 years due to expanding and intensifying agriculture and poor waste management. Between 5% and 12% of all greenhouse gas (GHG) emissions are produced by the extraction of

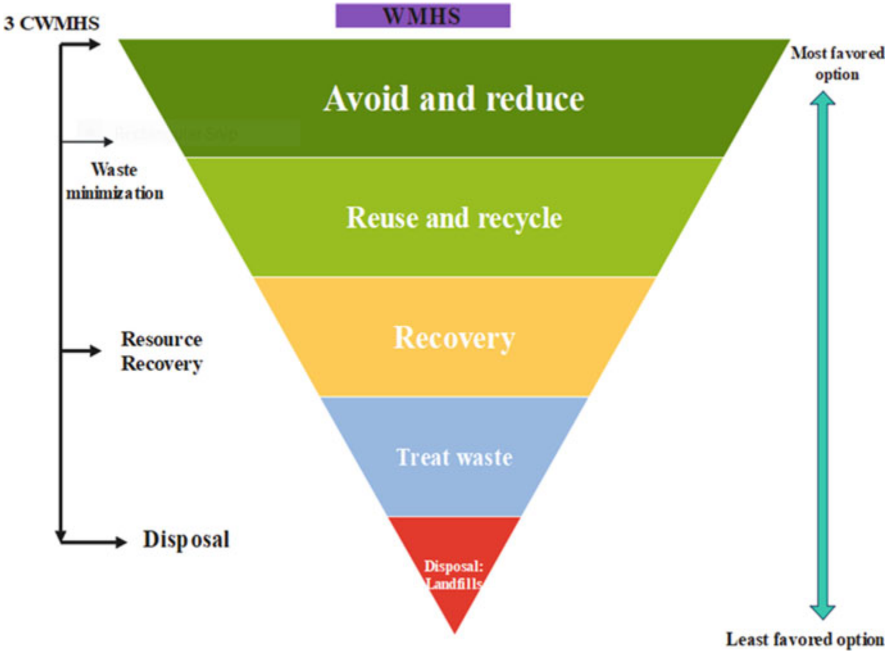

Fig. 1.2 The hierarchy of waste management and three core waste management systems

materials and construction products, both of which need vast quantities of energy. One of the biggest problems facing the building industry and other industries is the production and management of trash from agricultural industries. The primary crops are anticipated to produce over 3300 megatons of waste biomass. Construction accounts for 35% of all trash produced in the European Union (EU). The disposal and management of waste from these industries provide a significant issue in many nations, particularly from an environmental and social standpoint. The 2030 agenda featured 15 Sustainable Development Goals (SDGs), some promoting ecological and circular production and consumption to address the primary issues mentioned above. One of the key goals is also the management of trash, including agricultural waste. A priority input for new value-added products under the circular economy and bio-economy paradigms is agricultural waste biomass (AWB). This second-hand raw material's value addition produces financial gains. It substantially contributes to the sustainable use of natural materials by lowering dependence on nonrenewable resources and negatively influencing the environment (Duque-Acevedo et al. 2022).

Since it considers the larger economic, social, and environmental repercussions of a society's or community's waste system, many organizations, including educators, environmental groups, and industry and governments, frequently use the waste management hierarchy system (WMHS) (Fig. 1.2). The WMHS emphasizes waste prevention strategies as the preferable option, with trash disposal as the least preferred. The hierarchy is divided into three primary waste solutions in this chapter: waste minimization, resource recovery, and disposal (Doaemo et al. 2021). A sustainable method for managing agricultural bio-waste and developing a circular economy is the waste management hierarchy approach (WMHA), which places a higher priority on waste prevention, reuse, recycling, and material and energy recovery than disposal through landfilling. The most recommended strategy in agricultural waste management is waste prevention, which involves reducing the amount of garbage produced and extending a product's lifecycle to delay its entry into the waste category.

Moreover, hazardous waste substances must be reduced, and renewable resources must be used instead of nonrenewable ones throughout production. Additionally, it has been argued that preventative measures should include lowering consumer demand for particular goods and giving away goods to those in need. The goal of prevention is to avoid contaminating the ecosystem with toxic or nondegradable materials by preventing trash from entering the system (Kituku et al. 2020).

Waste recycling, any process in which non-waste items or components are used again for the intended purpose, is placed second in the waste hierarchy approach (WHA) of priorities. Rehabilitation operations are activities conducted to clean, repair, refurbish, and recondition items to prepare them for reuse. The growing trend toward seeing garbage as a resource rather than an issue that must be addressed has led to more attention being given to waste reuse. Legally classifying the majority of waste as trash that must be thrown away reduces the likelihood of reuse. The EU responded to the issue by designating recyclable waste as “end-of-waste” and “byproduct” status, respectively, and defining the conditions under which such materials stop being classified as garbage (REF). Recycling comes in third place and is defined as any procedure that turns waste into byproducts, materials, or substances that can be used for their original or additional uses. Recycling and recovery activities can result in new products with greater or lower objectives than the sources of waste.

The fourth priority in the waste hierarchy method is waste recovery, which entails actions intended to collect and use waste to augment other resources used for comparison purposes (WHA). Wastes can be recycled into new products or used as fuel for incinerators to recover energy. The discharge of GHG emissions and hazardous incinerator ashes are just two examples of the negative social and environmental side effects that persist even when recovery makes it possible to extract significant economic value from the trash. The lowest priority is disposal, which involves handling and getting rid of wastes for which there is no chance of recovery, recycling, or reuse. It is frequently accomplished by safely discharging waste into water bodies, incinerating it, and landfilling. This strategy is regarded as the least environmentally beneficial because of high fixed costs, material losses related to expenditures in necessary infrastructure, and environmental deterioration brought on by pollutants and leachates produced.

1.5 Agricultural Waste Management Techniques

The technologies discussed below will be able to accomplish excellent agricultural waste management concepts.

1.5.1 Landfilling

The simplest and most economical method of waste disposal is landfilling. It employs engineering principles to confine solid waste to the minimum area and the lowest volume allowable in a sanitary landfill (Muhammad et al. 2021). It is the most conventional and effective technique for disposing of solid garbage in many nations. Because landfilling is less expensive, labor-intensive, and designed for the safe disposal of solid waste, it is preferred to other municipal solid waste disposal options (Amran et al. 2021). Using efficient combined technologies to produce green energy and recycled materials, landfills can transform from "trash storehouses" to "energy powerhouses." The management of landfills is typically regulated by governments everywhere.

Depending on the type of waste, such as household garbage, biohazards, toxic chemicals, radioactive wastes, biomedical wastes, and building, demolition, and renovation wastes, landfills and remediation facilities are situated in various locations. Another way to categorize landfills is according to their intended use. Examples include bioreactor landfills, reusable landfills, monofillandfills, and secure landfills (Tsui and Wong 2019). Secure landfills enclose the wastes, delaying any detrimental environmental effects, while monofil landfills store wastes that cannot be handled through incineration, resource recovery, or composting. Reusable landfills allow waste to be stable for longer before being excavated to recover glass, metals, plastics, and compost. Lastly, bioreactor landfills are hygienic landfill sites with liners, leachate collecting, and recirculation systems that enhance microbe-assisted waste decomposition while minimizing environmental effects (Vaverková et al. 2020). Transportation costs, requirements of large land area, surface runoff during rainfall, and leachate are some limitations of landfill techniques.

Sanitary, semi-controlled landfills and open dumps are the three types of landfills (Nguyen et al. 2019). Municipal solid waste dumped in small open land with access to fresh air is called an open dump landfill. Municipal solid waste is negligently dumped in low-lying open areas in all developing countries, creating open dumps. A haven for scavengers like eagles, falcons, crows, vultures and other birds, pests, worms, rodents, and dangerous bacteria, these landfills are poorly managed and have become one such place. However, the lack of oxygen in anaerobic digestion eliminates these operational problems. Municipal solid waste is dumped at semi-controlled landfills, where it is first sorted, compacted, and minced before being disposed of. The discarded masses of waste are crushed and leveled using crawlers or bulldozers and enclosed with a cover of topsoil each day to minimize annoyances like the reproduction of scavenging birds, animals, bugs, and bacteria (Tsui and

Wong 2019). Topsoil covering makes semi-controlled landfills less smelly, but they are not made to limit leachate outflow or landfill gas emissions.

On the other hand, sanitary landfills are more advanced variants of semi-controlled landfills. It has the technology to capture gas emissions and collect liquid leachate, segregation, sorting, densification, size reduction, and topsoil covering (Nanda and Berruti 2021). The routine application of covered soil on top of freshly dumped trash distinguishes sanitary landfills and lowers odor, disease vectors, fires, and waste scavenging (Pujara et al. 2019).

1.5.2 Incineration

Along with bio-waste minimization and hazardous material destruction, incineration is one of the most often employed municipal solid waste processes. Individuals carry it out on a small basis, and businesses do it on a huge scale (Muhammad et al. 2021). This method is primarily based on high-temperature solid, liquid, and gaseous waste combustion. The most economical and practical way to eliminate hazardous trash, including medical waste, is through incineration. As a result of its lengthy history, incineration is regularly combined with heat and energy recovery systems, and these systems' values and efficiency have significantly increased in use. Separating bio-trash from municipal waste may be desirable because damp bio-waste lowers incineration efficiency (Harshwardhan and Upadhyay 2017).

Contrarily, the Renewable Energy Directive and the planned Directive on the Promotion of the Use of Energy from Renewable Sources both classify incinerated biowaste as a carbon-neutral "renewable" fuel (RES Directive) (Tsui and Wong 2019). The bulk of municipal solid waste incineration facilities burns this garbage raw. The technical term for this is mass burn (Nguyen et al. 2019). However, this process also releases carbon dioxide into the atmosphere, producing noncombustible elements like ash. Incinerators greatly reduce up to 90% of the volume and 75% of the weight of municipal solid waste (Tsui and Wong 2019). Because of worries about releasing harmful pollutants, flue gas treatment has evolved more in incineration than in ashes recycling or combustion processing (Kim et al. 2022). MSW can be viewed as a heterogeneous "fuel" that can be burned, with the main components (such as chlorine and sulfur) producing a poisonous and highly acidic flue gas. High concentrations of heavy metals and aromatic compounds, such as dioxins and furans, are frequently detected in the environment near incinerators when flue gas is improperly managed. When flue gas is not properly treated, it is common to find elevated amounts of heavy metals and aromatic compounds (such as dioxins and furans) in the area close to incinerators (Afolayan et al. 2019). Modern incinerators have numerous pollution control devices that trap nearly all of the pollutants that cause air quality issues, as well as the toxicity and disposal of the ash. Trace amounts of pollutants, such as certain metals, acid gases, and chemical compounds known as dioxins and furans, which have been linked to birth abnormalities and different types of cancer, are nevertheless released into the atmosphere (Tsui and Wong 2019). The price of land and the development of new incinerators are additional issues that many communities are worried about. The construction of an incinerator is frequently a municipality's single largest bond issue.

In most cases, incinerating is also more expensive than landfilling (Muhammad et al. 2021). They will have a cost advantage if landfills are available and legal. Incinerators become more cost-effective when cities cannot dispose of their trash locally in a landfill and must begin transporting it to distant sites (Salvilla 2020). The distinctive quality of incineration in managing heterogeneous trash is its robustness. Due to its age, incineration is currently most likely the best temporary "solution" for rapidly increasing population growth with solid waste generation (Tsui and Wong 2019). In addition, incineration has drawbacks such as high moisture contents, toxic metal concentration in ash, and low overall efficiency of small power plants.

1.5.3 Composting

Composting is one of the most popular methods for treating agricultural waste, which yields a product suited for soil amendment and is metabolically employed to kill pathogens in the thermophilic phase (Bian et al. 2019). Microorganisms such as protozoa, algae, fungi, and bacteria break down organic materials and create compost under carefully controlled environmental conditions (Mengqi et al. 2023). In composting, food scraps and garden trimmings from MSW are utilized as feed, and four key reaction steps occur (Tsui and Wong 2019). Popular aerobic composting techniques include sheet composting, aerated static pile composting, windrow composting, in-vessel composting, Berkley quick composting, and vermicomposting (De Corato 2020).

Crucial elements in the composting process include an area of land with appropriate aerobic conditions, compatible microbes, and the ideal temperature and moisture for microbe survival. The compost can be ready in 2–4 weeks to a few months. It is rich in nutrients and frequently used as a soil conditioner in horticulture, agriculture, and gardening (Bian et al. 2019). Applications for compost materials include building landfill covers, wetlands, land and soil reclamation, and soil erosion control. Composting reduces the volume of MSW and may transform this waste into a resource; hence it is highlighted that its application is both technically and economically possible (Chen et al. 2019). Ensuring microorganisms live in the best possible environmental conditions is the most challenging problem in this procedure. Other environmental problems with composting include acidification of the land, leachate leaks contaminating surface and subsurface water, odor, and health impacts from consuming contaminated water (Zhang et al. 2020). Composting can save landfill disposal costs, is suitable for various wastes, has fewer nitrogen contents, and reduces MSW carbon emissions by 20–25%, assuming environmental conditions remain steady. Nevertheless, composting has certain drawbacks, including the lengthy processing time, the vast amount of space needed for composting and storage, and the demand for high temperatures and excellent aeration for disease control.

1.5.4 Anaerobic Digestion

When organic matter is subjected to anaerobic conditions for digestion, the main byproducts produced are carbon dioxide and methane. It is possible to reuse the digestate as manure or a soil conditioner (Li et al. 2021). Notably, 55–60% of the methane fuel produced during this anaerobic process is used for various commercial and domestic uses. For hundreds of years, anaerobic digestion has been employed for hygienic purposes. It involves an all-encompassing, anaerobic microbial degradation of digestible organic materials (Wang et al. 2020). Anaerobic digestion produces more biogas in a shorter time than landfills, thanks to microbial activities comparable to anaerobic digestion. It has been demonstrated that the anaerobic digestion process produces 2–4 times more methane fuel per ton of MSW in 3 days than in a landfill in 7 days (Tsui and Wong 2019).

Organic wastes can be separated into solid and liquid using anaerobic digestion, resulting in solid and liquid digestate (Li et al. 2021). Based on the amount of water in the organic waste slurry, anaerobic digestion processes can be divided into two: a wet process containing 5% of total solids and a dry process containing greater than 20% of total solids (Pujara et al. 2019). The nutrients in the liquid digestate (mainly nitrogen and phosphorus) can be recovered using various bio-refinery methods, even though the liquid digestate volume produced by dry anaerobic digestion is substantially less than that produced by wet anaerobic digestion process (Chozhavendhan et al. 2023). Although anaerobic digestion is an advanced technology, research has continued to investigate how to get better quality effluent and make valuable links with other environmental technologies (Weide et al. 2020). Anaerobic digestion is sometimes hampered by the lengthy methanogenic reaction time required for biogas production, which normally takes 20–40 days for every normal batch and even more for a fresh new batch (Wang et al. 2020). However, nitrogenous wastes and excessive salts in the substrate would restrict the anaerobic digestion processes because of the raised levels of ammonia and salt, potentially resulting in anaerobic digestion system failure (Li et al. 2021). Another drawback of anaerobic digestion methods is their unsuitability for waste with a lower organic matter concentration and their demand for waste segregation to increase digestion efficiency.

1.5.5 Pyrolysis and Gasification

The thermal processes, such as gasification and pyrolysis, have advantages over conventional incineration in terms of higher thermochemical transformation efficiency (due to the different operating temperatures and other atmospheric conditions), which makes it easier to get recyclable byproducts and also can lower flue gas emission pollution (Tsui and Wong 2019). Alkali volatilization and bed agglomeration can be prevented by thermal treatment at lower operating temperatures. Other than waste incineration, none of the other thermal waste procedures for MSW is fully commercialized and is still in the early stages of research (Mengqi et al. 2023).

Although it requires higher operating temperatures between 300 and 1000 °C, pyrolysis is a thermochemical method for treating solid waste without oxygen. Char and condensable gases are desirable byproducts (Zhu et al. 2022; Costa et al. 2022). This alternative technique transforms MSW into value-added gas (non-condensable syngas), liquid (bio-oil), and solid commodities (biochar) (Zhu et al. 2022). The solid carbonaceous materials known as biochar can be utilized as a fuel, adsorbent, and catalyst. Low molecular gases in syngas, such as CO, H_2, CO_2, CH_4, and others, can be utilized after processing in gas combustion engines. Alcohol, phenolic compounds, aromatic and aliphatic hydrocarbons, and nitrogen-based substances like pyrazine, pyridine, amines and others make up the bio-oil, which can produce heat in boilers (Bhatia et al. 2021). Although pyrolysis has proven to be feasible for several selected feeds (usually agricultural waste), the variability of MSW makes the requirement for thorough MSW pretreatment a significant application problem. The feed materials and operating conditions significantly influence the production and composition of the gases/oils generated by the pyrolysis process from MSW (Adekanye et al. 2022). In majority of the time, operational temperature increases the overall MSW gas output. Still, it remains below 1 Nm^3/kg MSW, and the liquid products mostly comprise a sizable water portion and complex structured chemicals (Tsui and Wong 2019). These reasons lead to complex wastewater treatment processes before disposal, and the outcomes are insufficient in material cycling/energy. Plastic waste should be used rather than heterogeneous MSW bulk if oil production is needed. Even though MSW char has a high energy value and may be used as a source of solid fuel or material, further research is necessary due to the presence of hazardous heavy metals and organic pollutants (Harshwardhan and Upadhyay 2017).

At high temperatures (more than 700 °C) in an oxygen-poor atmosphere, a thermochemical process that transforms carbonaceous waste into gaseous fuel (CH_4, CO_2, H_2, CO, etc.) and traces of hydrocarbons is called gasification (Gabhane et al. 2020). Partial oxidation is accomplished using carbon dioxide as a gasifier agent instead of waste incineration. Dioxin, NO_x, and SO_2 generations are better regulated, and the overall amount of flue gases decreases, leading to low-cost gas treatment devices. The reduction of influe gas volume causes pollutants to concentrate, making physicochemical treatment that collects tiny particle matter more effective (Tsui and Wong 2019). Some MSW types, including paper waste, packaging waste, and plastic trash, have already undergone gasification. However, pretreatment is typically necessary for mixed MSW, and the mechanical biological treatments additional energy use should be considered when calculating the total energy balance. Fundamentally, the fluid, heat, and mass transfer and complicated chemical interactions are all involved in gasification/pyrolysis and other parallel and linked processes. Due to syngas conversion, a highly dependable control system is necessary to control syngas toxicity and potential for explosion; gasification is more challenging than waste incineration. Additionally, syngas is commonly consumed and lost during conversion, bringing the final energy production near waste incineration facilities. Due to operational complexity and underutilized energy enhancement, gasification for MSW cannot be used further due to these key concerns.

Table 1.1 Advantages and disadvantages of agricultural waste management techniques (Li et al. 2021; Muhammad et al. 2021)

Technology	Advantages	Disadvantages
Landfilling	Low cost	Transportation expenses are significant
	Skilled personnel not required	Required large land area
	Direct thermal usage and energy generation are both possible with the produced gas	Only 30–40% of the total gas is produced
	Can transform marshy areas into useful areas	Pollution is caused by surface runoff during rainfall
	Recycled natural resources are used, and the soil is replenished	The leachate may pollute the soil and groundwater
Incineration	It is appropriate for garbage with a high calorific value relatively noiseless and odorless	Required skilled workforce
	It requires low land	High moisture content
	Thermal energy for power plant	Toxic metal concentration in ash
	It can be found within the city limits	The high capital cost required
		The overall efficiency of small power plants is low
Composting	Suitable for a wide variety of wastes	Long processing time
	Contain less nitrogen	Does not address excess nutrient problems
	It increases the water content and retention of sandy soil	Large land required for compositing and storage area
	Cheaper than other means of disposing of wastes	Pathogen control requires high temperature and good aeration
	Higher yield and eco-friendly	
	Stabilities of organic components and nutrients	
Anaerobic digestion	Energy recovery by manufacturing superior soil conditioner that is odorless, rodent and fly-free, and visible	Unsuitable for wastes with a lower organic matter content
	It is feasible on a small scale	Requires increased pretreatment methods
	GHG emissions are reduced	Waste segregation is required to improve digestion efficiency
Pyrolysis and gasification	Fuel oil/gas production for several uses	In trash with too much moisture, net energy recovery could be compromised
	Pollution control is superior to incineration	The high viscosity of pyrolysis oil may make it difficult to burn and transport

Gasification and pyrolysis may be challenging to burn and transport due to the high viscosity of pyrolysis oil. Table 1.1 below lists the benefits and drawbacks of agricultural waste management methods.

1.6 Health and Environmental Impact

Agricultural production waste that is burned or decomposed in an open area emits gases, mixes with airborne particles and volatile substances, and seepage causes chemical and biological contamination of the soil and groundwater (Ayilara et al. 2020). It is impossible to overstate the effects of this cause on the ecosystem, animal health, climate change, and human health. To prevent the imminent threat to the planet, earth, and its inhabitants, as well as a temperature increase of at least 35.6 °F, for instance, it has been suggested that greenhouse gas emissions be substantially curtailed. Figure 1.3 indicates the environmental and health effect of agricultural waste.

Methane and nitrous oxide emissions from animal husbandry are more harmful than CO_2, accounting for between 37% and 65% of global emissions. Greenhouse gases are released when agricultural solid waste is burned carelessly. Food production is hampered by improper agricultural solid waste management since it contributes to climate change (Amran et al. 2021). The consequences of indiscriminate agricultural solid waste disposal cannot be overstated. Additionally, a significant amount of methane (a greenhouse gas) is produced during the breakdown of organic waste, which is a factor in the increase in global temperatures and alteration of climatic conditions. Additionally, the high organic component of MSW encourages the proliferation of microbes that can cause infectious and chronic

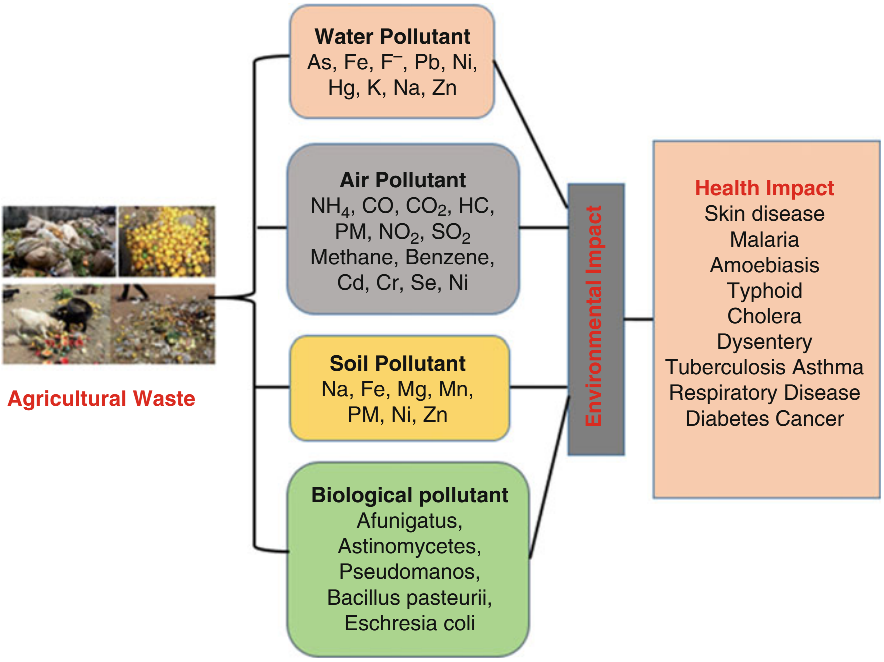

Fig. 1.3 Effects of agricultural waste on the environment and human health

illnesses in garbage employees, rag collectors, and adjacent residents. Burning MSW or pathogenic microorganisms can result in various health issues, such as gastrointestinal issues, allergies, skin irritation, eyes and nose irritation, respiratory system irritation, and psychiatric difficulties.

1.7 Conclusions

Due to the severe environmental effects of inappropriate disposal, agricultural waste management has become crucial. Wastage, underutilization, lack of awareness, and poor treatment are the primary causes of agricultural waste pollution. Most farmers are unaware of the advantages and financial possibilities of waste recycling. The transformation of agricultural wastes into value-added byproducts has attracted great interest in recent years because of the growing demand for goods with natural additives and stricter environmental laws. Additionally, recovering resources from agricultural waste can minimize waste generation and reduce new resource usage by transforming waste into readily available resources. Recent developments in the idea and production, characteristics, hierarchy of agricultural wastes approach, and various important management practices, including landfilling, incineration, composting, anaerobic digestion, pyrolysis, and gasification, were discussed. Agricultural wastes must be considered potential resources rather than undesirable and unwanted.

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Global Status of Agricultural Waste-Based Industries, Challenges, and Future Prospects

2

Aishi Nath, Krishna Das, and Ganesh Chandra Dhal

Abstract

To battle unemployment, poverty, water shortages, and political ramifications, a worldwide emphasis and effort have been placed on the growth of agriculture. Animal husbandry, food processing, irrigation, harvesting, transport, and crop storage are instances of agricultural processes. These activities generate a million tonnes of organic and inorganic waste annually, including crop leftovers, animal manure, and chemical and biological fertilisers. Agricultural wastes should be properly handled to prevent major environmental issues such as eutrophication of surface water, groundwater pollution, odour emissions, and soil, water, and air degradation. Bioactive compounds are abundant in agricultural residues. Many commodities, including fruits, rice, sugarcane, corn, coffee, soybeans, and many others, are abundantly produced around the world. These operations generate massive amounts of daily residues like coffee peel, sugarcane bagasse, and rice husk. Agriculture-dependent countries must prioritise the reuse of agricultural and agro-industry waste to turn a profit by reusing the waste rather than just disposing of it. These residues can be used as raw material in various researches and industries to come up with new products such as biofuel, biogas, animal feed, antioxidants, construction material, mushrooms, tempeh, and other chemicals. Utilising these wastes minimises trading fossil fuels and other agro-based agrochemicals. Most countries misguide or discard agricultural waste due to either neglect or an absence of an effective channel to transfer and implement it. Using agricultural waste as a raw material can help reduce production costs while lowering environmental pollution. This article may very well discuss the

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global status of agricultural waste-based industries, the obstacles they face, and the sector's prospects in the decade (2011–2022).

Keywords

Agro-wastes · By-products · Rapid growth · Urbanisation · Challenges · Waste reuse

2.1 Introduction

The global misuse of nature's resources through various human endeavours, such as population growth, industrialisation, and urbanisation, has led to a notable rise in the generation of various types of waste (Obi et al. 2016). Different types of waste and its by-products are produced in tonnes each year by various industrial, agricultural, and other activities, with waste from agricultural practices being one of the more noticeable and prevalent types (Dai et al. 2018). Agriculture is the largest industry producing biomass, and it is also the oldest and most widespread occupation in the world (Kuthiala et al. 2022; Singh et al. 2022). Over the last five decades, agricultural production has increased threefold. In addition to urbanisation, the green revolution's technological advancements and soil expansion for agriculture are two other variables that could boost agricultural output (Duque-Acevedo et al. 2020; Adejumo and Adebiyi 2020; Food and Agriculture Organization of the United Nations (FAO) 2017). To fulfil the current demands of the growing human population, various modern agricultural techniques have greatly expanded food production, which now stands at about 23.7 million foodstuff tonnes per day worldwide (Food and Agriculture Organization of the United Nations (FAO) 2017). Despite the benefits of agricultural development and progress, there are several clear drawbacks, including resource exploitation, environmental pressure, and adverse effects on human health, soil, and water (Kuthiala et al. 2022).

Agriculture as a whole has prioritised crop production above livestock output. Small farms traditionally use crop leftovers, plant residue, and a variety of agro-industrial by-products as feed sources, but advances in nutritional science offer chances to improve their feeding properties (Yunus et al. 2020). Nowadays, biomass derived from agricultural waste is increasingly used to create energy due to its high energy conversion potential. The use of agricultural waste is growing relevant, especially in light of the estimated global energy demand gap. A new opportunity has come to light as the agro-waste could be used for energy production giving a chance to increase agricultural activity. In certain regions of India, husks, weeds, and other agricultural wastes which were considered worthless are being revolutionised into sustainable, non-polluting, and inexpensive energy. In 2016, research demonstrated the viability of using coffee grounds in the construction of bricks and wheat bran in the creation of bio-alcohol. Due to rapid urbanisation and industrialisation, a huge amount of heavy metal is produced, and this needs treatment. In recent years, agro-waste has been used to treat heavy metals, which pose a threat to the environment. Low-cost agricultural waste such as rice husk, oil palm shell, sugarcane bagasse, sawdust, neem bark, coconut husk, etc. has been used for the treatment of heavy metals from wastewater (The Sentinel 2023, n.d.).

According to statistics, more than 12 billion tonnes of refuse are produced yearlong globally, with Asia alone producing more than 5 billion tonnes of it (Atinkut et al. 2020; Dhar et al. 2017). In developing nations like India, where industrialisation, urbanisation, population expansion, and food production are all expanding rapidly, the generation and management of agricultural waste are becoming difficult, posing environmental and social risks (Atinkut et al. 2020; Dhar et al. 2017). Agro-waste consists of waste from processed food (fruit pulps, packing materials and by-products), agricultural leftovers (such as tea, sugarcane bagasse, paddy, husk, maize stalks, leftover vegetables, jute fibres and fruit peels), lethal wastes (such as insecticides and pesticide runoff) and animal wastes (such as manure and dead animals) (Obi et al. 2016). Generally agricultural waste is not toxic, but its enormous production and poor management pose serious hazards to overuse of the soil, climate change, the creation of greenhouse gases, global warming and pollution of the land and water (Manna et al. 2018). An innovative strategy of turning agro-waste into electricity has recently been introduced for waste management (Prakash et al. 2018; Noman et al. 2020). The 3Rs idea (reuse, reduce, and recycle) and other strategies including waste minimisation, landfilling, decomposition, composting, and bio-digestion are included in the sustainable strategy to manage agro-waste. The conventional waste management practice is the disposal of waste without treatment in landfills which results in air pollution, pesticide runoff, and water pollution. Among the various organic and inorganic components found in agricultural leftovers are the three primary polymers cellulose, lignin, and hemicellulose (Bhuvaneshwari et al. 2019). The next sections discuss in-depth agro-waste, its classification, composition, global status, handling, and potential future developments.

2.2 Agricultural or Agro-Waste

The term "agro-waste", which refers to agricultural waste, is used to describe wastes generated by various agricultural operations, such as irrigation, agriculture-based industrial produce, farming, cattle breeding, slaughtering, etc. These wastes include manure, abandoned raw materials, fertilisers, by-products, field overflow, polluted water, and soil that contains silts, pesticides, heavy metals, and salts. For around 58% of the population in our country, agriculture, the largest biological sector, provides the majority of their jobs. A rise in the level of living, including a need for basic food and medical facilities, is faced by developing nations like India, China, Africa, and others in addition to a growth in population. Consumption and waste production both rose along with this inflated demand (Atinkut et al. 2020; Manna et al. 2018; Kuthiala et al. 2022). To create a system that effectively manages waste, it is essential to understand the various waste categories that have been covered below, the constitution of agricultural waste, and how they can be beneficial to the environment.

2.2.1 Agricultural Solid Waste Classification

The primary source of agricultural waste is farming. Stages of the agricultural-food chain can produce a large amount of agricultural solid waste. Agriculture-related solid wastes fall under the following general categories:

2.2.1.1 Livestock Waste

Solid wastes produced by raising animals, for any purpose. These wastes include water troughs, animal carcasses, broken feeders, bedding, and litter.

2.2.1.2 Waste from Food and Meat Processing

Harvest and animal products from slaughterhouses such as banana peels, hoofs, feathers, bones, and other wastes falls under this category.

2.2.1.3 Waste Generation Through Crop Production

Waste from the crop is generated from agricultural activities that involve crop production like crop leftovers and husks.

2.2.1.4 On-Farm Medical Waste

Waste produced as a result of using medications, immunisations, pesticides, herbicides, or animals and crops. Such wastes include, for instance, vaccination wrappers, disposable needles, containers, syringes, etc.

2.2.1.5 Waste from Horticulture

These solid wastes from agriculture are produced when horticultural plants and landscapes are grown and maintained for aesthetic purposes. Pruning and grass clippings are two examples of these wastes.

2.2.1.6 Waste from Agro-Based Industries

Livestock and agricultural products are raised and produced for purposes other than food use. They are put to other purposes; thus, it is likely that these processes will produce agricultural solid wastes. A little amount of agricultural solid waste is produced during the paper-making process when agricultural products are used as raw materials.

2.2.1.7 Chemical Wastes

Agricultural wastes, such as pesticide bottles or containers, supplied when farmers use pesticides, insecticides, and herbicides on farmland and in stores (Dien and Vong 2006; Obi et al. 2016; Adejumo and Adebiyi 2020).

The following sections provide a better understanding of the composition of agricultural waste and its by-products.

2.2.2 Composition of Agro-Waste

It is essential to understand the fundamental makeup of agricultural waste to implement efficient management solutions. Figure 2.1 shows the structural makeup of the agricultural waste residues which are lignocellulosic material with a partly crystalline compact structure made up of cellulose, lignin, hemicellulose, organic materials like oxygen, hydrogen, carbon, nitrogenous materials, etc. and inorganic materials like silica, calcium oxide, etc. These materials are used as building blocks in other types of materials. The majority of this biomass contains cellulose, lignin, and hemicellulose which are raw materials for secondary value-added products. Understanding the structural components of the biomass is required to utilise these residues, as will be addressed further (Bhuvaneshwari et al. 2019; Kuthiala et al. 2022).

2.2.2.1 Cellulose

Glucan chains, which are made up of a succession of glucose units, form the polysaccharide known as cellulose. Cellulose is linear and crystalline, with its crystalline structure provided by the glucose units bonded together by -1-4-glycosidic linkers. Cellulolytic enzymes can quickly convert cellulose into less complex

Fig. 2.1 Agricultural waste residues (Kuthiala et al. 2022)

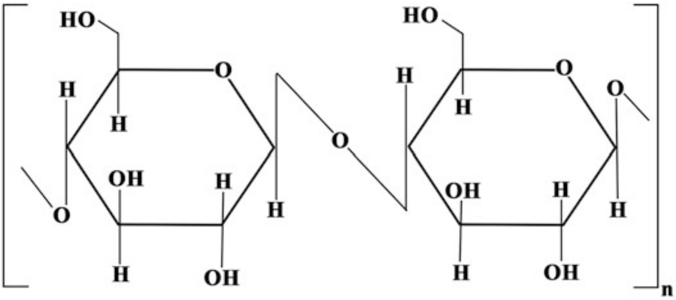

Fig. 2.2 Molecular structure of cellulose

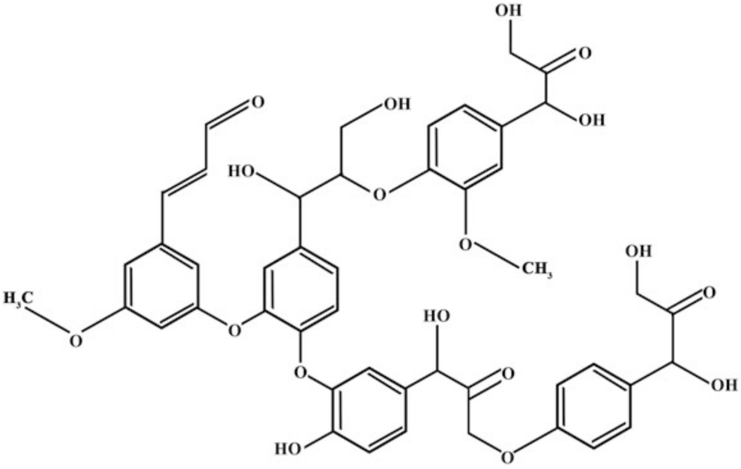

Fig. 2.3 Proposal for the molecular structure of lignin fragment

monomeric carbohydrates (Wakade et al. 2015). Figure 2.2 shows the molecular structure of cellulose.

2.2.2.2 Lignin

It is a naturally occurring branched non-crystalline aromatic polymer produced in plants via the shikimic acid route from three monomers: sinapyl alcohols, *p*-coumarin alcohol, and coniferyl alcohol. It contains various functional groups, including methyl, carbonyl, and hydroxyl. Lignin is impregnable and provides structural support, making it resistant to degradation by chemical and biological processes, in contrast to hemicellulose and cellulose (which can be broken down by enzymes) (Wakade et al. 2015; Kuthiala et al. 2022). Figure 2.3 shows the proposal for a molecular structure of lignin fragment.

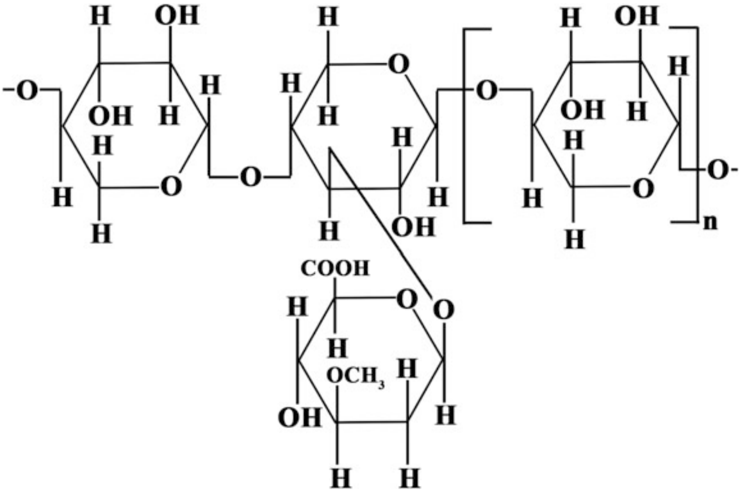

Fig. 2.4 Molecular structure of hemicellulose

2.2.2.3 Hemicellulose

It is a hetero-polysaccharide that is non-crystalline, non-cellulosic, and branched. It is composed of a variety of linear and branched polymers, including glucose, galactose, xylose, arabinose, mannose, and methyl and other acetyl groups that are variously linked to the carbon chain of hemicellulose. The cellulose and hemicellulose components of agricultural residue structure are bound together by lignin (Wakade et al. 2015; Kuthiala et al. 2022). Figure 2.4 shows the molecular structure of hemicellulose.

2.2.3 Agro-Waste By-Products

Agro-waste by-products are of various types, including by-products from crop waste and residue, grain and legume milling industry, sugar, starch, confectionary industry, fruit and vegetable processing industry, distilleries and breweries, and oil industry. Generally, the kind of by-product dictates the methods and technologies employed for its processing (Ajila et al. 2012).

2.2.3.1 Value-Added Products

Adding value to agricultural byproducts increases their marketability and economic value. A significant amount of cellulosic material is contained in agricultural by-products, which, when recycled, enriches the soil with nutrients and carbon. Its high nutritional content makes it suitable for waste conversion to bioenergy and biofuels. Economic benefits include an increase in farm goods while lowering production costs, and the adoption of agricultural resource use, so transforming farming into a viable occupation. Thus, employment is created, by-products are disposed of in the environment, and the environmental quality is improved (Ayoo and Bonti-Ankomah 2019; Koul et al. 2022).

2.2.3.2 Utilisation of the By-Products

In past centuries, farmers dumped agricultural by-products into the environment, thereby polluting it. As soon as they realised the value of these by-products, the value of animal feed and fertilisers, and the detrimental environmental impact, they began to use them as animal feed. Agro by-products play an important role in boosting the nutritional content of animal feed since they are rich in macro- and micronutrients required for body growth and production (Shamsi et al. 2012; Alam et al. 2014). Increasing the use of agricultural by-products can provide a sustainable foundation for rural small- and medium-sized companies and stimulate rural economic development. Using crop residues as manure and biofertilisers, in addition to raw materials for producing energy and consumer goods, may raise the profitability of agricultural businesses, improve environmental quality, and promote energy security (Tiwari and Khawas 2021).

2.3 Cause of Agricultural Waste Production

Production of agricultural solid wastes is primarily caused by agricultural activities that entail the storage, handling, processing, production, and intake of agricultural goods, livestock, and their by-products. The following are some reasons why agro-waste is produced.

2.3.1 Agriculture-Related Activities

Agriculture is the main contributor to the generation of agro-waste. This waste is produced during every stage of farming operations, from preparing the land for farming to harvest (Agrawal et al. 2019).

2.3.2 Poor Road Infrastructure Sustainable Solid Waste Management Techniques

An inadequate road network used to transport harvested products from the farm to the market or storage facility also contributes to the production of massive volumes of agricultural solid waste. This is mostly caused by the poor road infrastructure in some developing nations, which may cause traffic accidents or cause delays in the transportation of agricultural products from farms to markets (Imran-Shaukat et al. 2022). On the route to the market, the farmer either separates the spoiled product for disposal or throws it away once there.

2.3.3 Insufficient or Non-existent Rural Electrification

The development of agro-waste is greatly influenced by the epileptic power supply and the absence of rural electrification in several emerging nations with major agricultural activity (Patel et al. 2022). Stable electricity might have made it easier to store the harvested food in the cold, reducing spoilage and, as a result, agricultural solid wastes.

2.3.4 Improper Drying Processes and Storage Facilities

With the right drying methods, much agricultural produce may be protected from spoiling. Farmers could have prevented ago-waste, improved food security, and food spoilage, lessening the ill effects of waste on human health and the environment. Farmers rely heavily on the erratic solar system for drying the production before storing it (Yuan et al. 2015). They also use the outdated, ineffective approach of conventional moisture monitoring. Aflatoxin contamination has been linked to inadequate moisture monitoring of grain before storage. Aflatoxin contamination of livestock feed and food can result in considerable worldwide crop losses annually (Klich 2007; Nierman et al. 2015; Adejumo and Adebiyi 2020).

2.3.5 Food Wasted

Another significant source or cause of agro-wastes is food spoilage. When fruits and vegetables purchased are so rotten or damaged that they are no longer edible, spoiling occurs. There is a tremendous quantity of food waste in restaurants and at street food stands, where people consume and discard leftover restaurants (Pagliari et al. 2020). Apart from this, kitchen waste also includes the everyday food spoilage that happens in households. An estimated 40% of food is discarded or wasted each year in the USA alone. The Natural Resources Defence Council has calculated that this waste will cost around 162 billion dollars (Adejumo and Adebiyi 2020).

2.3.6 Kitchen Waste

Kitchen-generated agricultural solid wastes are typically a by-product of family consumption of agro-based products. Skins of fruits and vegetables are frequently disposed of as agricultural solid wastes in houses. However, inadvertent production of agricultural solid wastes can also occur when food spoils. When restaurants are counted as kitchens, the amount of agricultural solid waste produced by kitchens increases (commercial kitchens) (Li et al. 2016).

2.4 Global Status of Agro-Waste

An age-old practice agriculture has undergone steady changes with the rising standards of living and population increase. Significantly, agro-industry focuses on the production of value-added goods by manufacturing diverse agricultural products and by converting inedible, large, and fragile raw materials into the desired shape, safe, edible foods or beverages with the desired quality (Chhetri et al. 2020).

The global population is declining, but some regions will experience growth beyond 2050 and into the next century. Every year, at least 1,300,000,000 metric tonnes of agricultural waste are generated, and the number is anticipated to increase as the world's population grows (Lee et al. 2022). The agriculture industry produces more than 24 million tonnes of food annually to fulfil the requirements of a growing global population. Cities have a higher population density than rural ones, and it is expected to expand exponentially. Rapid urbanisation has changed nourishment patterns, which has had an impact on increasing agricultural production (Afolalu et al. 2021). The agricultural sector alone provides 24 million tonnes of food globally, along with associated health and environmental risks. Farming is still the primary method of producing food and other crop- and animal-derived products required for modern living (Bhatt and Singh 2018). The Food and Agriculture Organization (FAO) of the United Nations is crucial in ensuring that the needs of the entire population—across age groups, regions, and urban and rural areas—are met in terms of food and agriculture. As shown in Fig. 2.5, the United Nations Population Divisions have forecasted population growth in three scenarios: low,

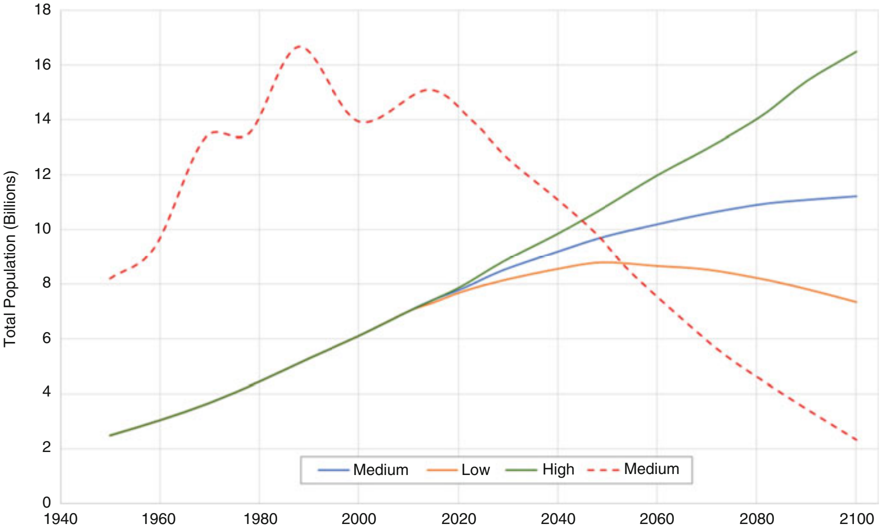

Fig. 2.5 Global population based on variants until 2100. The annual increments are a 5-year average. (Source: da Silva 2017)

medium, and high. The medium variant will be the primary focus of subsequent analysis (Food and Agriculture Organization of the United Nations Rome 2017).

2.4.1 Overall Population Growth

The late 1960s saw a growth rate of 2%, the highest of that decade. In 2015, there was a 2.5 reduction in the total fertility rate (TFR), resulting in a 1.2% annual decline in the world's population. The medium variant is projected to decline by 55 million by 2050, and this trend is expected to continue until the end of the century. By 2050 and 2100, respectively, the world's population is projected to reach 9.73 billion and 11.2 billion, due to this gradual increase in population. However, disparities between and within regions, as well as low-, middle-, and high-income countries, are likely to mask this global trajectory of development. High-income countries are expected to reach their peak population by 2040, while low- and middle-income nations are more likely to see a decline in their populations, with significant variations in growth rates within low-income countries. Asia, the most populous continent, is projected to reach its peak population between 2050 and 2060, as shown in Fig. 2.6.

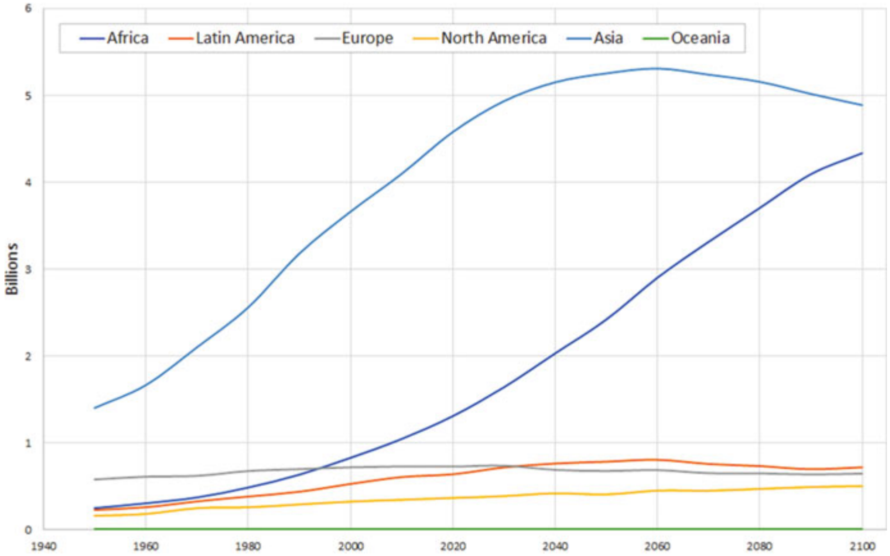

Fig. 2.6 Regional population growth through 2100 (medium variant). (Source: da Silva 2017)

2.4.2 Medium Variant Population Growth

The population growth rate in East Asia is anticipated to continue to decline after 2040. South Asia will not stop expanding until 2070; its peak will not come until after that. Latin America's population will not reach its peak until after 2060, and growth there is also anticipated to slow, albeit more gradually. The Near East and North Africa are expected to experience faster and more resilient growth, with growth ceasing only after 2080. The maximum population size will not be attained on any other continent of this century except Africa. The population of the region is anticipated to continue expanding past the turn of the century and will surpass 2.2 billion by 2050 and 4 billion by 2100, even though its growth rate will continue to decline. The overall result will be a continuously expanding global population that may approach 11.2 billion by 2100. Even more so than disparities across regions, differences within regions are noticeable. According to current projections, the population of some nations will increase so quickly that, by 2050, it will be multiples of what it is today. Niger tops the list of countries with rapidly expanding populations, with growth rates of 3.75% between 2015 and 2050 and 2.12% afterwards predicted.

According to the medium variant, the population of Niger would increase from its current 20 million inhabitants to 72 million by 2050 and 209 million by 2100. Somalia, Angola, the Democratic Republic of the Congo, Burundi, Gambia, Chad, Malawi, Uganda, Mali, the United Republic of Tanzania, Senegal, and Zambia are all expected to experience annual growth rates of over 2.5% cent through 2050. Most of these nations are found in the central and eastern regions of sub-Saharan Africa, where they are located. In 2015, 320 million people were living in these countries collectively. By 2050 and 2100, that number is expected to more than double, totalling 1.8 billion people. The chances for these countries' overall development could be substantially jeopardised if these population estimates come true. The fact that the above countries significantly rely on agriculture for employment and revenue generation puts at risk efforts to improve food security and nutrition. This is especially true for nations like Niger and Somalia, which are dependent on agriculture and have a limited supply of land and water. In low- and middle-income nations, the population between the ages of 15 and 24 is anticipated to increase from roughly 1 billion to 1.2 billion between 2015 and 2050. It is anticipated that the majority of these young people would reside in South Asia and sub-Saharan Africa, particularly in rural regions with few employment opportunities.

This population trend could result in an increased rate of emigration if there are not enough employment opportunities. Some emigration destinations are already experiencing the effects of outmigration, both domestically and internationally, particularly in high-income countries in other regions and Europe. Family planning may help to partially stop these outmigration trends (Abbasi and Abbasi 2010). However, policies that support respectable employment and income-generating options, particularly in rural areas, are more crucial.

2.4.3 Effects Due to Rapid Urbanisation

Several decades ago, the majority of the world's population resided in rural areas. Thirty-five years ago, more than 60% of people lived in rural areas. The ratio of urban to rural areas has significantly changed since then, with metropolitan areas currently accounting for around 54% of the global population. In 2050, or 35 years from today, more than two-thirds of all people may reside in metropolitan areas (da Silva 2017). Urbanisation is being supported by changes in agriculture, particularly in terms of technical development and the introduction of labour-saving technologies. The effects of urbanisation have also and will probably continue to have an impact on agriculture, food, and nutrition. By 2050, the net addition of 2.4 billion people to urban areas owing to global urbanisation may exceed the 2.2 billion increase in the world's population. This implies that rural communities could experience a net loss of roughly 200 million individuals (Fig. 2.7).

The net decline in rural populations is due to several variables, most notably greater mortality rates and shorter life expectancies in rural areas, rather than just an emigration from rural to urban areas. The lower urban fertility rates are more than countered by these elements. Up until the 1970s, urbanisation was mostly a phenomenon of high-income nations, but since then, the dynamics of urbanisation around the world have been characterised by rapid expansion in low-income nations. The dynamics of the world are currently governed by a large number of urban residents in low-income countries (Fig. 2.8).

In low-income countries, urbanisation is predominant, but the clear view is veiled in various regions. Latin America has often been the world's most urbanised developing region. Particularly in South America, urbanisation happened quickly and early. The region's population was categorised as urban by more than two-thirds by 1980, and that percentage increased to about 85% by 2015. However, due to its

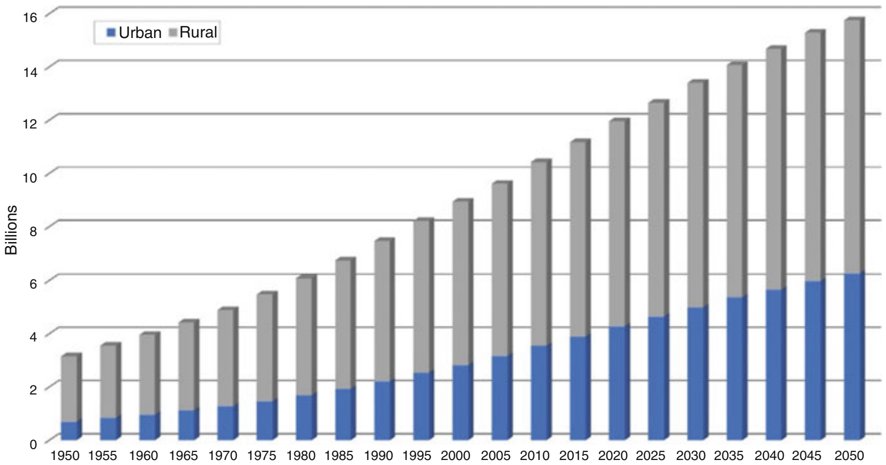

Fig. 2.7 Population growth in rural and urban areas worldwide by 2050. (Source: da Silva 2017)

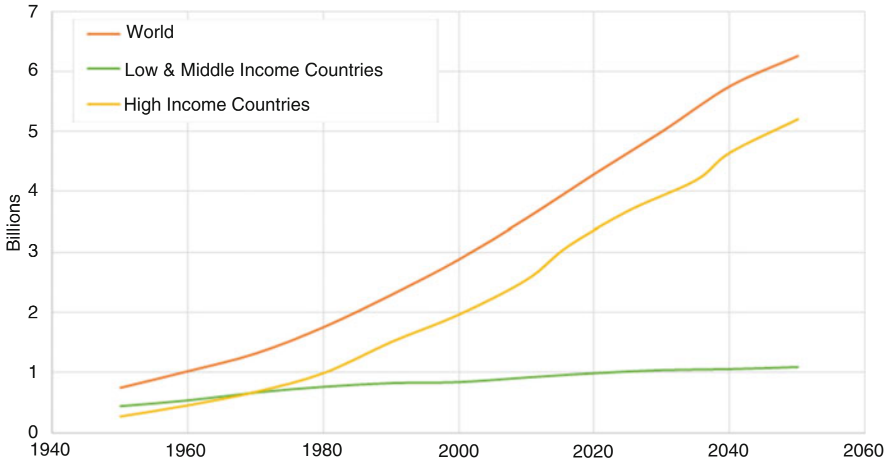

Fig. 2.8 Regional trends in urbanisation

high level of urbanisation, future growth will remain modest and urbanisation rates will drop, but in less urbanised areas, urbanisation rates may increase (Chanakya et al. 2015). Patterns of food consumption are impacted by urbanisation. Higher urban prosperity tends to boost demand for processed meals as well as food produced from animals, fruits, and vegetables as part of a general dietary trend. Higher opportunity costs for food preparation and a preference for meals with a high labour content, such as foods made and sold by street vendors, convenience foods bought at stores, and fast food, are typically caused by higher urban wages (Food and Agriculture Organization of the United Nations (FAO) and Organization for Economic Co-operation and Development (OECD) 2019).

Recycling agricultural solid wastes has several advantages, including reduced usage of fossil fuels and greenhouse gas emissions. Additionally, it benefits the development of bioenergy generation and the bioconversion of agricultural solid waste into animal feed and new green markets (Abbasi and Abbasi 2010). The following sections highlight the challenges posed by agro-waste production.

2.5 Management of Agro-Waste

Selective yet efficient management techniques are needed for agricultural waste among many various types of waste. Huge volumes of agro-waste are produced annually; their composition, types, and sources must be adequately examined and classified to develop a management strategy (Aïzi and Cheba 2015). Since agro-waste is a leading environmental concern, it must be managed sustainably. A sustainable waste management strategy is therefore put into place, which includes production standards like composting, reusing, and recycling, as well as the creation of industrial ecosystems with no emissions, waste minimisation, and waste prevention (Koul et al. 2022; Kuthiala et al. 2022).

The handling of agricultural waste is a common and complex task that affects both the economy and the environment (Duque-Acevedo et al. 2020). A typical agricultural waste management system (AWMS) is a method to use, process, and store waste. The system is divided into six major categories, each of which has a clear and defined goal (Bhatt and Singh 2018): (1) production, (2) collection, (3) transfer, (4) storage, (5) treatment, and (6) utilisation make up this list of separate elements (USDA-NRCS-Agricultural Waste Management field handbook). Recognising the elements that make up a waste management system is essential to learning more about how it was designed:

2.5.1 Production

Determining the density, mass, consistency, quantity, origin location, and composition of the refuse produced is the first and most important step in designing a waste management system (agricultural waste). By using cutting-edge methods that are practical for particular waste kinds, the goal is to minimise waste from the very beginning of production (Atinkut et al. 2020).

2.5.2 Collection

The following phase, after thoroughly analysing the manufacturing parameters, is to gather the garbage from the source or location of origin. A key stage in classifying waste into clearly defined and useful parts for treatment or management is the manner and method of collecting agro-waste (Koul et al. 2022). Collection dates, labour needs, installation cost, manner of collecting, and use of external resources are a few elements of a collection (Bhatt and Singh 2018).

2.5.3 Transfer

The relocation or transfer of the waste is the subsequent management phase after collection. The transfer must be implemented throughout the management system in several steps rather than just in one. Waste must be transported from the collecting place, which might be a field or a food processing plant, to the storage containment, which varies based on the nature and characteristics of the agro-waste, such as solid, gas, or liquid, and then to the treatment facility (Bhatt and Singh 2018).

2.5.4 Storage

According to the type, location, and method of treatment of the waste, storage is the containment area that can be put up anywhere (Pagliari et al. 2020). The cost of the facility, the amount of storage space required, the total amount of waste to be stored, and physical store parameters (carbon dioxide levels, oxygen levels, humidity, airflow, and temperature) can all have an impact on the storage process, consistency and nature of the waste, and the necessary amount of time (Bhatt and Singh 2018).

2.5.5 Treatment

The treatment phase of AWMS is crucial. The primary objective of waste treatment is to limit the waste's potential for contamination or make it simpler to utilise the detritus as a modified value-added product in the future. To design the appropriate treatment for specific wastes, it is vital to analyse the waste's characteristics, including its composition, size, cost, treatment type, and design procedure (Bhatt and Singh 2018). Composting, incineration, and landfills/dumping are the traditional treatment methods. On the other hand, more cutting-edge, environmentally friendly approaches to waste treatment have been adopted, such as the production of biocompounds like biodiesel, biochar, and bioethanol from agro-waste (Manna et al. 2018).

2.5.6 Utilisation

The AWMS protocol's final stage, known as the process of utilisation, is conceptually the recycling of waste materials using the previous step of treatment. Utilisation's fundamental tenet is the repair and redistribution of waste components to create new products with added value (Chatterjee and Bandyopadhyay 2017). The goal of recycling garbage into secondary products is to reduce waste production across all industries, led solely by agriculture. The varied agricultural wastes can be converted into a variety of value-added products depending on their composition. Biogas, biofuel, biopolymers, nutrients (such as single-cell proteins), and charcoal are the main products made from agro-waste. Kiwi peels, banana peels, watermelon shells, and honeydew peels are examples of agricultural wastes that can be turned into biochar and biosorbents with few pre-treatment processes and minimal chemical exposure. Agro-wastes are transformed into activated carbons to prevent them from increasing BOD (biochemical oxygen demand), COD (chemical oxygen demand), or TOC (total organic carbon) levels when used directly to remove heavy metals (Imran-Shaukat et al. 2022; Agrawal et al. 2019).

2.6 Challenges of Agro-Waste

The emission of greenhouse gases related to agro-waste generation in Greece was studied by Abeliotis et al. (2015), and according to the researcher, each person generates 100 kg of waste annually.

The consequences of the Integrated Waste Management facility of Barcelona, Spain, on human health were studied by Domingo et al. (2015) as per the data incinerator emission were ten times higher than in other areas. To reduce the environmental risk adverse needs to be taken.

Repercussions on the environment due to the production of electricity and composting of agro-waste have been studied by Elwan et al. (2015) who concluded that agro-waste used for electricity generation could reduce the discharge as compared to composting practice.

The environmental impact due to biogas facilities was studied by Fuchsz and Kohlheb (2015) who found that anaerobic digester that takes agro-waste as their raw material acts as a carbon dioxide absorber.

Environmental monitoring of clinker production using two fuels in Mexico was studied and concluded that co-processing with agro-waste has a low impact compared to petroleum coke. An alternative material in agro-waste management can be refuse-derived fuel (Güereca et al. 2015).

Life cycle emission management was used to assess the impacts of matrix material qualities, product consumption, and waste management system (WMS) on the anticipated environmental concentration (PEC). According to the statistics, the counterintuitive jumped when PEC levels were 2.6% (Wigger et al. 2015).

Based on biogas-generating scenarios, the environmental effects of agro-waste were analysed, and it was seen that the use of fossil depletion, freshwater eutrophication, marine ecotoxicity, and human toxicity was good for the ecosystem (Yang et al. 2015).

2.7 Future Prospects of Agro-Waste

Agro-waste is a valuable resource for the production of a variety of value-added goods, including fuel, feed, environmentally safe chemicals, bioactive compounds, protein sources, and substrates (enzymes derived from agro-waste) (Noman et al. 2020). Agro-waste serves as an affordable substitute for industrial adsorbents for heavy metals since it is organic and cheap. Aside from the numerous ways that agro-waste can be converted into secondary products through biological conversion, they are widely employed as substrates to manufacture selective sets of enzymes in a variety of industrial processes, in place of pricey commercial counterparts. Due to their better adsorption capacity, high surface reactivity, and high porosity, activated carbons made from agro-waste can be good bio-sorbent substitutes for commercial adsorbents (Yunus et al. 2020). To lower the cost of the process, oxidative enzymes such as lignin peroxidase, laccase, and manganese peroxidase were produced from *Aspergillus iizukae* by submerged fermentation using pumpkin peels (agro-waste) as the substrate (Noman et al. 2020). To achieve structural and toxicological changes, the key saccharification and hydrolysis steps of biomass use are where enzymes or biocatalysts come into play. As a result, they play a significant role in agro-waste management. Like any other process, enzymatic bioconversion has its share of drawbacks in addition to its benefits. Parameters that are widely categorised as either enzyme-based or physical, both of which affect the hydrolysis efficiency of employed enzymes, may modify the conversion processing (Wakade et al. 2015).

There are many opportunities for future advancement after reviewing the extensive studies of enzyme-based agro-waste treatment technologies. The goal of the research is to create more specialised enzyme blends from fewer, rather than more, organisms, to decrease production costs and turnaround times. In the parts that follow, a few repercussions of food waste are discussed.

2.7.1 Renewable Energy Resources

Agro-waste rich in organic components, particularly polysaccharides, can be specifically directed towards the manufacture of ethanol since its hydrolytic by-products, such as xylose and glucose, are converted to ethanol (Prasoulas et al. 2020). High moisture, organic contaminants, and salinity are present in food waste from restaurants and residential rubbish (Singh et al. 2022; Saeed et al. 2018). Currently, food industries produce enormous amounts of lignocellulosic by-products from the production of wine, beer, sugarcane, coffee, drugs, fruits, and vegetables. These by-products are typically discarded as waste, and when they are disposed of in the open place, they frequently cause environmental pollution. The large variety of husks, pulp remnant stems, roots, bagasse, seeds, and peels that make up these by-products are rejected by the industries while having high nutritional potential (Gómez-García et al. 2021). It is significant to note that there are various substrate types and classifications for the manufacture of ethanol. The first category includes molasses and fine sugar, which microorganisms may convert directly into ethanol without the need for any labour-intensive preparation. However, due to their high volume, these substrates are not economically viable for industrial application. Crops like wheat, corn, rice, etc., which can lead to a food and feed crisis, are included in the second group of substrates. Lignocellulosic biomass, often known as agricultural surplus, is the third group of substrates and requires pre-treatment before being hydrolysed enzymatically to produce fermentable sugar, which is then used to ferment ethanol. Food waste can replace the third category of the substrate (agricultural residue), which is used in the production of second-generation ethanol because it has a high amount of carbs and organic material. Enzymatic hydrolysis is the second stage after pre-treatment to make biomass accessible to enzymes in the process of vapourising carbohydrate-rich food waste to create bioethanol. The main goal of the pre-treatment process is to change the chemical content and molecular structure of biomass.

According to research by Highina et al. (2014), using biofuels lessens the influence of greenhouse gases by 78–94%. Hydrogen, biogas, bio-methane, syngas, bioethanol, biochar, and biodiesel are all energy products that can be produced from biomass and their by-products. Both power plants and vehicles can employ liquid biofuels. Coal can be replaced by solid biofuels. As was already noted, animal and livestock wastes can result in gaseous biofuels (biogas and bio-methane) that can be used in the production of electricity. Producing fine and bulk chemicals as well as other useful biomaterials using biomass and its by-products as feedstock is feasible (Go et al. 2019).

2.7.2 Biofertilisers

The impacts of chitinous waste on *Triticum durum* (wheat) rhizospheric bacteria had a substantial influence on the soil's microbiota and pH when wheat soil was mixed with varying amounts of chitinous waste. Extracted from shells are valuable substances like proteins and chitin. After cellulose, chitin is the second most prevalent polymer in the biosphere (Aïzi and Cheba 2015).

By providing nutrients and readily available carbon, sheep bedding digested with cow dung enhances the output of the biogas and biofertiliser by-products of anaerobic digestion. The results demonstrated that a combination containing 50% cow dung boosted biogas production and enhanced the quality of biofertiliser (Cestonaro et al. 2015).

Chatterjee and Bandyopadhyay (2017) discovered that micronutrients are essential for cowpea development, pod formation, and nodulation in acidic soil. The results demonstrated that a combination of seed treatment, molybdenum (0.5 g/kg seed), biofertilisers, and foliar spray of boron boosted the growth and yield of cowpea by 42% and 55%, respectively.

Mondal et al. (2017) observed the bio-physiochemical change in the characteristics of mustard by integrating biofertiliser with vermicompost. It was observed that vermicompost altered the majority which was tested by lowering chemical fertiliser by 25% and integrating it with vermicompost.

2.7.3 Soil Amendments

The impacts of biochar (B) and compost (Com) on peanut productivity, soil fertility, and greenhouse gas (GHG) emission were compared on the Ferralsol Australian using B, Com, B + Com, or COMBI which enhanced soil organic carbon (SOC) while reducing greenhouse gas emissions, soil nutrient, peanut output, and soil water content (SWC) (Agegnehu et al. 2015).

Various soil amendments applied in the agricultural field of the Republic of Korea, Japan, and Bangladesh discovered that these amendments would greatly reduce global warming potential (GWP). To minimise GWP in equatorial and subtropical locations, it is recommended to combine *Azolla*-cyanobacteria with inorganic and organic inputs (Ali et al. 2015).

2.7.4 Dye Adsorption

Agricultural by-products can be utilised for dye adsorption. Adegoke and Bello (2015) used agricultural wastes to extract the dye. The results indicated that 4–5 h was the optimal time for absorbing colours from agricultural waste. In conditions of pH 8–10, agricultural wastes were capable of absorbing the greatest number of acidic dyes.

Bhatnagar et al. (2015) evaluated the effect of agricultural waste peels processed as multifunctional biomass for water purification. They also discovered that there was a significant demand for the application of agricultural waste peels in water. Waste peels, which could be utilised as lignocellulosic materials with a substantial amount of biomass, were extremely advantageous for boosting the yields of adsorbents for water management.

El-Bindary et al. (2015) removed harmful azopyrazole colour from water using rice straw. In addition, they investigated the various variables as a function of solution pH, reaction duration, adsorbate combination, adsorbent dose, and temperature. The results indicated that ACRS might be utilised as a renewable, low-cost material to remove acid dyes from water.

2.7.5 Heavy Metal Adsorption

To remove heavy metals like zinc, cadmium, nickel copper, and lead from contaminated soil compost-derived humic materials are considered an alternative for soil remediation from contaminated soil (Kulikowska et al. 2015). Biodegradability and biocompatibility of polymer-based adsorbents are important properties of water absorption. Renewable alternative adsorbent for heavy metal removal from an aqueous environment is magnetic chitosan/cellulose microspheres. Different agro-wastes can be used as biosorbents to remove heavy metals using biomass and acidic solutions (Rosales et al. 2015). Differential thermal analysis (DTA), a process of forming metal compounds by mixing biosorbents with metals, is an effective alternative for heavy metal removal (Sadeek et al. 2015).

2.7.6 Energy Recovery from Agro-Waste

Agricultural waste that is disposed of without adequate treatment can produce greenhouse gases that damage the environment during decomposition. However, agro-waste can also be used as a type of biomass waste that absorbs thermal energy through thermochemical conversion to generate usable biofuels such as liquid biofuels (biocrude), gaseous biofuels like methane (CH_4) and carbon monoxide (CO), and solid biofuels like biochar. During the thermochemical conversion of agro-waste, exhaust pollutants such as particulate matter (PM), CO, hydrocarbons, and NO_x can be emitted. Sophisticated air pollution and wastewater treatment facilities can be used to control these pollutants to comply with environmental protection standards (Richards et al. 2012; Gómez-García et al. 2021).

Incineration is used to minimise waste volume, while combustion is used to create heat energy. Combustion is the process in which biomass waste is introduced into a high-temperature environment with sufficient oxygen to break the bonds of organic molecules and release CO_2 and H_2O into the atmosphere. Direct combustion is the technique used for generating energy from biomass waste, accounting for 90% of biomass energy, and it requires moisture content to be less than 50%.

2.7.7 Construction Materials from Agro-Waste

There has been recent emphasis on sustainable development and the adoption of eco-concrete in response to the increasing global population. The concept of a green economy, which is critical for both the environment and society, is becoming a growing concern among researchers. Large amounts of raw materials and natural resources are required for concrete production worldwide, while significant agricultural waste disposal poses significant environmental challenges. Agro-wastes can serve as a reliable alternative supplementary cementitious material. Decades ago, waste and by-product materials such as palm oil fuel ash, fly ash, silica fume, rice husk ash, and pulverised granulated blast slag were effectively used in concrete, contributing to the environmental sustainability of the industry by reducing the negative effects of raw material consumption (Aprianti et al. 2015).

The successful use of agricultural waste as a partial or complete replacement for Portland cement offers a satisfactory solution to environmental issues and waste management problems, conserves energy, and helps prevent environmental pollution. Agricultural wastes such as rice husk ash, wheat straw ash, sugarcane bagasse ash, and hazelnut shell ash can be used as pozzolanic materials to substitute for cement (Aprianti et al. 2015). Cement production is a significant contributor to global warming, causing climate change. The use of agricultural waste as a replacement for cement may be the breakthrough needed to make the industry more sustainable and environmentally friendly. Many forms of agricultural waste, such as rice husk ash, palm oil fuel ash, bamboo leaf ash, maize cob ash, wood waste ash, and sugarcane bagasse ash, can be partially substituted for cement. Thus, improving current knowledge of the use of agricultural waste in concrete production and exploring alternative options for sustainable building and environmental protection will be a beneficial contribution (Aprianti et al. 2015).

2.8 Conclusion

It is essential to develop a comprehensive waste management strategy that considers factors such as public health, public awareness, economics, and environmental protection. The agricultural sector globally provides over 24 million tonnes of food to meet the needs of the expanding world's population. Agricultural waste accounts for about 15% of each country's total waste production and is a significant contributor to environmental contamination, making proper treatment and sustainable disposal crucial. Decomposed food waste presents health hazards and contributes to environmental contamination, and its rate of growth is alarming alongside the population. Therefore, reducing food waste during production is crucial. Another method of addressing this issue is to use food waste as a raw material for producing value-added products, such as bioethanol, as it is a suitable source based on its composition.

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3

Technoeconomic and Sustainability Analysis of Agricultural Waste Conversion Technologies

Rejeti Venkata Srinadh and Remya Neelancherry

Abstract

The rise in the world's population, combined with the expansion of agricultural practices and the processing of food, has resulted in an increase in the production of waste from agricultural practices, as well as challenges with its management. Converting agricultural waste (AW) and crop leftovers into useful forms can help alleviate some of the problems caused by the massive amount of waste produced by these activities. The conversion of this waste into biofuels continues to be an alternative that is both environmentally friendly and economically practicable. One of the most promising methods of turning biomass into biochar, biooil, and syngas is microwave-assisted pyrolysis (MAP). It is very important to carry out a technoeconomic analysis (TEA) and a life cycle assessment (LCA) before attempting to transform a lab-scale microwave reactor into a commercial plant. This will allow one to gain an understanding of the economic feasibility of the project as well as the environmental implications it will have. This chapter focuses on the concept of circular bioeconomy emphasising the technoeconomical aspects of MAP for bioenergy production from agricultural waste. It also discusses briefly the parameters and challenges involved in both batch and continuous MAP techniques. Further, this chapter examines the environmental performance of agricultural waste via life cycle assessment of biofuel generation with several MAP approaches. Various waste utilisation routes of life cycle assessment illustrate the potential of each residue in terms of impact categories such as global warming potential, eutrophication potential, acidification potential, etc.

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Agricultural waste · Biomass · Microwave-assisted pyrolysis · Technoeconomic analysis · Circular bioeconomy · Life cycle assessment

3.1 Introduction

Rapid growth in human population and industrialisation leads to the increased demand for fooding and energy sources, respectively. This increasing demand for food leads to the growth of agricultural practices across the world. On the contrary, the agricultural practices envisaged eventually increase in various types of agricultural waste generation. In order to incorporate agricultural practices in limited amount of land, the wastes generated are generally open burnt in many of the developing countries like India resulting to greenhouse gas (GHG) emissions and climate change (Koul et al. 2022). The need for new renewable energy sources and agricultural waste management can both be satisfied by the conversion of these biomass wastes into bioenergy products. There are various techniques for the bioenergy production like thermochemical processes (gasification, incineration, torrefaction, pyrolysis) and biochemical processes (anaerobic digestion, fermentation) (Arpia et al. 2021). Agricultural wastes are readily available, renewable, and sustainable. It is neutral in terms of carbon emissions, as burning emits the equivalent amount of CO_2 into the surroundings to that of photosynthesis that absorbs CO_2 for biomass plant development. Consequently, the use of biomass for bioenergy production will also benefit human health and ecology (Durga et al. 2022). Employing waste from agricultural as a raw material for biofuel production lowers dependency on forest woody biomass, hence reducing deforestation. Thermochemical conversion routes present potential opportunities for the utilisation of mostly dry wastes like rice straw and rice husk. This chapter intends to convey a summary of recent thermochemical conversion processes, specifically microwave-assisted pyrolysis (MAP), for the production of biofuels from agricultural by-products and to analyse the scalability of this technique for generation of circular bioeconomy by technoeconomic analysis and life cycle assessment of different kinds of agricultural waste in different MAP conversion technologies.

3.2 Agricultural Waste: Source for Bioenergy

The production of biofuels from agricultural waste, also known as agro-waste (AW), is gaining a lot of attention since it has numerous options for effective waste management as well as numerous energy benefits. Globally, agricultural activities generate vast quantities of agro-waste, notably in developing countries. The production of agricultural waste biomass around the world is estimated to be close to 140 billion metric tonnes. As an agricultural nation, India produces around 0.62 billion tonnes of agricultural waste yearly, of which hardly 25–30% are utilised for

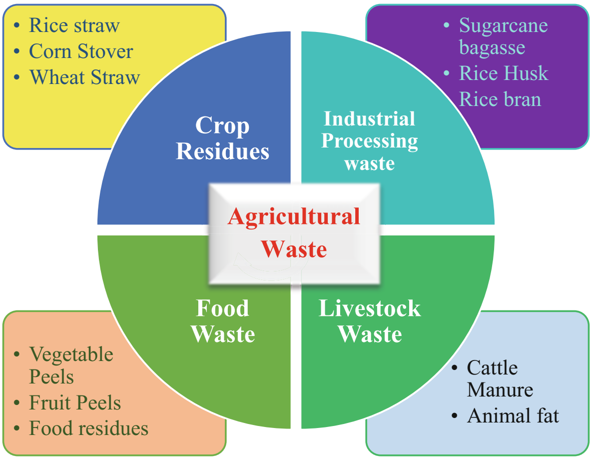


Fig. 3.1 Agricultural waste classification

livestock feed and bioenergy production (Matsagar and Wu 2022). The classification of agricultural waste is depicted in Fig. 3.1. On-farm agricultural waste is referred to as cellulose and hemicellulose which includes waste products such as straws, stalks, and leaves. These waste products come from agricultural or farming processes. The crop processing processes result in the production of agro-food waste, the quantity of which varies greatly depending on the types of plants processed. The properties of this waste play an important role in determining whether or not they can be used in bioenergy production (Singh et al. 2022). Most agricultural wastes are made up of lignocellulose, a multicarbohydrate polymer consisting of lignin, cellulose, and hemicellulose. To employ biomass feedstocks with significant differences in composition, a deeper understanding of the effects of these three key components is required. The decomposition of biomass is typically associated with the disintegration of lignin, cellulose, and hemicellulose. Components like hemicellulose and cellulose break down readily compared to lignin, at the lower temperature range of 220–350 °C. Lignin is the most resistant constituent of plant cell walls, which comprise a natural barrier that guards against the chemical and enzymatic breakdown of plant cells, amongst key constituents of biomass feedstocks (Darmawan and Aziz 2022).

3.2.1 Major Organic Constituents

Cellulose: The majority of plant cell walls are composed of cellulose, which is the most prevalent type of organic polymer. Cellulose is a homopolymer which is both linear and crystalline and is made up of repeated units of sugars that are bonded together by beta-1,4-glycosidic linkages. Because van der Walls forces and hydrogen bonds hold the extensive linear cellulose polymer chain together, the chains have a tendency to organise themselves in parallel and create a crystalline structure. This network of cellulosic polymers contains approximately 10,000 glucose units. A cellobiose unit is the basic repeating unit of cellulose. It consists of two units of glucose anhydride (Rahimi et al. 2022). Cellulose and hemicellulose are the primary components in the production of biooil.

Hemicellulose: It is a heavily segmented short heteropolymer having an approximate molecular weight of 30,000. It is found in the cell walls of plants and other organisms. It is a polymer made up of D-arabinose, D-mannose, D-galactose, D-glucose, and D-xylose, in addition to specific organic acids including glucuronic and acetic acids (Takara et al. 2010). Hemicellulose is a polymer that is both branching and linear, and it has a base that is made up of sequences of either a heteropolymer of sugars or homopolymer sugar. Hemicellulose differs from cellulose in a few other ways as well, alongside the variations in chemical composition, such as the chain's size, segmentation in the main chain molecules, and chemical resistance due to amorphous nature (Arpia et al. 2021).

Lignin: Lignin, in contrast to cellulose and hemicellulose, is not made up of carbohydrate or sugar molecules but rather phenyl-propane compounds joined in a very intricate three-dimensional structure. Three different phenyl-propionic alcohols that are found primarily as lignin monomers are namely sinapyl alcohol, *P*-coumaryl alcohol, and coniferyl alcohol (Bajpai 2020). It is an aromatic biopolymeric compound that is hydrophobic in its natural state and has a large molecular weight. Cellulose and hemicellulose are strongly associated with lignin through covalent and hydrogen bonds, which makes the structure of the biomass robust and extremely resistant to both biological and physical assaults. It serves to block the entrance of other solutions or enzymes during bioenergy production processes and thereby turns to be an essential component in the synthesis of biochar (Rahimi et al. 2022).

3.2.2 Biofuel Production from Agro-Wastes

Despite the fact that various other techniques like combustion, liquefaction, gasification, etc. exist for the thermochemical decomposition of lignocellulosic wastes, pyrolysis is preferred because it makes more efficient use of the biomass' energy potential, produces less NO_x and SO_x contaminants than combustion, obtains a better biofuel yield with less energy consumption than conventional methods, and uses reduced pressure and produces comparatively lesser tar than hydrothermal liquefaction (Varjani et al. 2021). Pyrolysis requires an oxygen-free setting, which can be achieved with the help of inert atmosphere such as argon, nitrogen, carbon dioxide, vacuum pump, etc. The by-products of this process have a wide range of potential uses; for example, biooil and syngas can be synthesised to create motor fuels and other biochemicals, while biochar is typically used to improve soil properties and sequester carbon footprints. Biochar is ideal for a range of applications in the field of environmental management due to its exceptional properties, which include the presence of functional groups, large surface area, high porosity, and significant stability, presence of metallic cations and minerals, and good cation exchange capacity (Suriapparao and Vinu 2021). Because of the rising global demand for agriculture, food, and energy, soil degradation has also emerged as a critical issue. Using biochar in the soil to improve its quality is a viable solution to this issue.

Apart from being used as a sustainable fertiliser, biochar has certain qualities similar to coal and thus can be utilised as a solid fuel. It can also be used to treat high-strength wastewater by eliminating heavy metals, making the solution safe for reuse (Chen et al. 2020).

3.3 Microwave (MW) in Bioenergy Production

Energy can also be extracted from biomass by using the microwave-assisted pyrolysis (MAP) technique. When compared to traditional electrical heating processes, the benefits of microwave-assisted technology are numerous. These benefits include more uniform heating at the molecular level, more adaptable processes, more portable equipment, less thermal inertia, a quicker response time, and significant energy savings (Suriapparao and Vinu 2021). In contrast to the process that occurs during conventional heating, the energy conversion that takes place during microwave irradiation effectively leads to the production of volumetric heat within the target material (feedstock) rather than heat being transferred via the surface of the feedstock. Microwave-assisted thermal energy is evenly distributed throughout the material due to the direct conversion of electromagnetic energy into thermal energy at the atomic scale (Ge et al. 2021). Important biomass properties considered for microwave-assisted bioenergy production are particle size, density, and dielectric properties of the feedstock. Preheating, drying, blending, crushing, and inerting biomass are the most common pretreatments seen in microwave pyrolysis (Thengane et al. 2022). In order to achieve dielectric permittivity values that are compatible with wave penetration and propagation, drying is essential especially. The real and imaginary components of dielectric characteristics both increase when there's a considerable amount of water in the mix (Shukla et al. 2019). Humidity has both benefits and drawbacks for energy conversion to heat: on the one hand, it increases losses, which is good for the process, but on the contrary hand, it raises the dielectric constant, which causes high reflections and reduces wave transmission into the feedstock. Consequently, humidity regulation of the feed biomass is an important process control variable in microwave pyrolysis. As a second benefit, drying refines the quality of the final product. Biooil and syngas have a greater calorific value when less water is present in the process (Yang et al. 2018). This quality is commercially relevant if biooil is developed for use as a fuel source. Naturally, crushing and blending are helpful for maximising the homogeneity of the processed biomass. Crushing also helps the drying process because it lessens the constraint of water transport via internal diffusion. An anaerobic atmosphere for pyrolysis is ensured via inerting, which involves flowing a replacement gas from the feed hopper, such as nitrogen, to replace oxygen.

Largely, biomass waste has a high range of dielectric constants leading to lower dielectric properties, making them almost transparent to microwaves. This adversely affects the penetration and conversion of electromagnetic energy of microwaves into

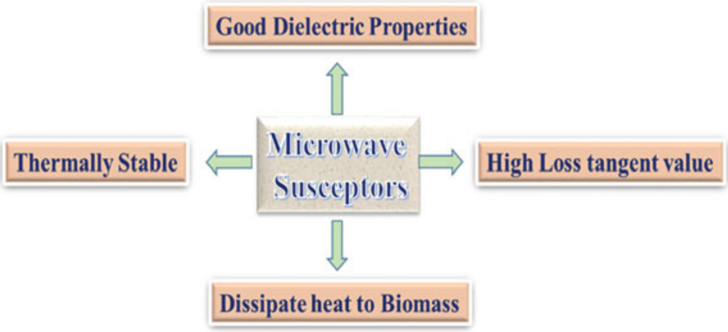


Fig. 3.2 Advantages of microwave susceptors in MAP

heat energy. Generally, microwave absorbers/susceptors like SiC, activated carbon, biochar, etc. are additionally provided within the reactor along with the feedstock to overcome the abovementioned drawback. The advantages of microwave susceptors are depicted in Fig. 3.2. Water, being polar in nature, has also been investigated as a microwave absorber since it enables the pyrolysis process to initiate at a considerably lesser temperature of approximately 200 °C. It is vital to note that the usage of water may only be encouraged if its implications on biooil constituents are thoroughly understood. The upgrading process uses a lot of energy and is consequently costly, but it turns biooils with a high moisture content into better quality fuels which have the ability to be utilised in engines. The activated carbon utilised as a microwave susceptor accelerates the heating process and enhances the specific surface area of the resulting biochar. Additionally, it was determined that thus formed biochar utilising activated carbon has been more reliable, that is, complete carbonisation of the feedstock was attained, leading to a biochar with greater energy content. The biggest disadvantage is the utilisation of biochar throughout the process of pyrolysis, which changes the quality and composition of the end products. However, the necessary dielectric qualities will dictate the percentage of biochar that must be recycled (Suriapparao et al. 2022).

By inducing rapid pyrolysis, MAP intends to circumvent some of the drawbacks of more traditional heating methods. In order to meet these criteria, it is necessary to optimise the feedstock processing time, heat distribution within the feedstock, and heating efficiency through the volumetric transfer of energy. In addition, MAP's adaptability stems from the wide range of possible operational settings. The pyrolysis mechanism is controlled by numerous factors, like pyrolysis temperature, type of feedstock, feedstock weight, microwave power, microwave susceptor type and loading, and feedstock/susceptor ratio (Shukla et al. 2019). The quality and distribution of the products can be optimised by controlling these variables.

In microwave-assisted pyrolysis of AW, the presence of different catalysts can change the amount of product yields with selective preference to biochar, biooil, or syngas generation more specifically. The catalytic microwave pyrolysis is expected to tailor the biochar to improve the fertility, water retention, sorption, and characteristic qualities in addition to increasing the biochar yield by encouraging coke formation. Multiple catalysts working together synergistically to increase microwave absorption result in a less acidic, reduced moisture content biooil. The availability of carboxylic substances in biooil, including acetic and benzoic acids, is thought to be the cause of its acidity (Neha and Remya 2021). It is possible to get a greater pyrolysis temperature for better dehumidification when catalysts are present (which also act as microwave absorbers). Steam reforming of oxygenates is another factor responsible for the low water and acid content of biooil (Gollakota et al. 2018). The creation of biooil is favoured over syngas and biochar as a result of the quick pyrolysis that results from the microwave absorbent properties of metal-oxides, salts, and acid catalysts. Different catalysts can modify the process of pyrolysis for improved syngas production during MAP of AW at the deterioration of the biochar and biooil yields. Throughout microwave pyrolysis of AW, catalysts encourage secondary heterogeneous processes to increase syngas output. Yet the catalyst stability with time, resistance to mechanical stirring, and ease of reuse are essential for the MW pyrolysis process, as they represent additional operational costs associated with separating and reusing the catalyst from the char (Mohamed et al. 2022). The cost-benefit analysis of its expansion into industrial/commercial scale is still in its early stages of research (Neha et al. 2022).

3.3.1 Continuous Microwave-Assisted Pyrolysis (CMAP)

Continuous microwave-assisted pyrolysis (CMAP) is an advanced method that can realise continuous large-scale feeding at high temperatures and carries the potential of increasing the quality and yield of different biofuels, thereby overcoming the limitations of batch scale MAP, which suffers from lower resource and energy efficacy. Table 3.1 summarises the bioenergy production from AW using both batch and continuous MAP techniques. The size of the AW feedstock that is packed within batch mode reactors for the pyrolysis is constrained by the reactor dimensions, which results in a poor processing rate. Reduced energy efficacy is the outcome of batch pyrolysis, which combines sample heating with time set aside for condensation, outflow, and reloading procedures. It is appealing to move from batch to continuous microwave pyrolysis of AW because the latter provides a quicker conversion rate along with less energy consumption (Ge et al. 2021). In order to address the drawback of the batch feeding method, the continuous MW reactor is hailed as a new potential approach for MAP of AW (Luo et al. 2021b). AW could be delivered to a continuous reactor via gravity as well as mechanical means, primarily by using a conveyor belt, rotary kiln, or an auger conveyor. The production of biochar in rotary kilns ensures better blending and heat transfer between several AW, but there are certain limitations, including lengthy residence periods, uneven power intensity, and a lack of sufficiently cold conditions for biooil condensation (Siddique et al. 2022). Although it is challenging to find extremely thermostable belt material, conveyor belts are favourable because of their greater and consistent power

Table 3.1 Microwave-assisted bioenergy production processes from agricultural waste (Iturbides et al. 2022; Ge et al. 2021; Luo et al. 2021b; Shi et al. 2020)

Biomass	Lignocellulosic content (%)			MW pyrolysis technique	MW susceptor	MW power (W)	Temperature (°C)	Time (min)	Inert gas	Catalyst	Particle diameter (mm)	Mass/feeding rate	Product yields (%)		
	L	C	HC										S	L	G
Corn Stover	14.5–18	27.0–48.3	27.00–37.0	Continuous	NA	750	490–560	NA	V	NA	0.9–1.9	NA	NA	64.0	NA
Sugarcane bagasse	13.0	50.0	29.0	Batch	NA	NA	500	30	N_2	NiO	0.25	3–5 g	15.5	34.5	50.0
Switchgrass	12–28	32–45	21–31	Batch	SiC	750	400	20	N_2	K_3PO_4	NA	20 g	43.7	29.3	27.0
Rice husk	12–29.3	15.5–26	28.7–40.0	Batch	NA	700	600	50	N_2	Cu/RHC	NA	50 g	47.0	12.0	50.0
Pinewood sawdust	30.97	40.32	26.73	Batch	SiC	1000	470	15	N_2	HZSM-5	NA	15 g	26.7	17.3	56.0
Bamboo	11.9	53.1	35.0	Batch	SiC	3000	600	15	N_2	AC	0.2	5 g	22.8	0.3	76.9
Pine	11.2	59.1	29.7	Batch	SiC	3000	600	15	N_2	AC	0.212	5 g	23.5	2.2	74.3
Coconut shell	50.0	20–30	15–30	Continuous	NA	5000	500	NA	NA	NA	20–40	350 kg/h	31.0	35.0	34.0
Peanut soapstock	28.0	37.0	18.7	Continuous	SiC	800	400	NA	V	HZSM-5	0.25	0.3 kg/h	22	47.68	30
Wood pellets	31.0	40.0	12.0	Continuous	SiC	1500	800	NA	V	NA	7.3	0.2–10 kg/h	NA	NA	73.30
Cow manure	NA	40.0	12.0	Continuous	SiC	0–4200	650	NA	N_2/CO_2	NA	0.074	NA	NA	NA	71.02
Douglas fir	34.1–67.2	15.9–38.3	16.5–27.0	Batch	NA	650	300	NA	N_2	NA	NA	200 g	49.61	17.4	33.25

L lignin content, *C* cellulose content, *HC* hemicellulose content, *S* biochar yield, *L* biooil yield, *G* syngas yield, *V* vacuum
RHC rice husk char, N_2 nitrogen gas, *AC* coconut-derived activated carbon, *NA* not available/not specified

density, lesser incubation times, and steady regulation of relatively lower thermal inertia. A greatly localised power density distribution is produced by the auger conveyor because the rotation encourages heat transmission between the feedstock, pyrolysis products, and reactor wall. To efficiently extract biooil and syngas, an auger system is advised for feedstock input and biochar output. However, the auger system has some drawbacks, including the need for long-lasting auger materials and the significant biooil fouling of the auger surface (Luo et al. 2021a). CMAP has the potential to be a very efficient industrial application, but all it requires is the proper understanding of the energy conversion and pyrolysis mechanisms involved which is presently very limited.

3.3.2 Limitations and Challenges Involved

There are certain potential challenges for the CMAP to be fully available for commercial or industrial applications in terms of bioenergy production:

1. Agricultural waste comes in different forms and have a wide range of properties. Since feedstock properties play a major role in final product yield both in terms of both quantity and quality, it is very essential to define the operating parameters of the MAP process accordingly (Ge et al. 2021).
2. Another difficulty in continuous microwave pyrolysis is the design of a material handling system to input the biomass and discharge the biochar. The thermal expansion of the auger causes it to grow in size relative to other systems (like a belt conveyor) when operating in hot conditions. However, the input and outflow rates can be regulated by adjusting the auger's speed, allowing for limited control of the microwave pyrolysis time period. For microwave pyrolysis, a vertical shaftless auger should be created in the long term to propel the feedstock from the top down (Siddique et al. 2022).
3. It is very important to reduce heat loss during the separation of biochar from volatile biofuels (biooil and syngas). Effective condensation systems and biochar collection systems should be simultaneously working, so that the condensable compounds or tars shall not get in contact with the biochar thus produced (Iturbides et al. 2022).
4. There is always a potential for the development of hot and cold areas within the microwave reactor chamber due to improper propagation of microwaves. In order to decrease the likelihood of hotspots forming in the feedstock, it may be beneficial to integrate the use of numerous MW magnetrons additionally fitted with mechanical stirrers to provide the vortex action in the pyrolysis chamber.
5. The belt carrying the feedstock and/or the biochar within the pyrolysis chamber must be capable of withstanding high heating rate and temperatures. This condition limits to the usage of either metals or ceramics even for industrial applications (Ge et al. 2021). Further research can be focused on developing economic alternatives, to reduce the overall cost of production at large scale.

6. The produced hot vapours during the biochar production can be recirculated into the reactor to maintain the required temperature instead of operating the magnetron at lesser power levels for the same. Reducing heat losses and making use of waste energy are two ways in which the process can be energy optimised, both of which are essential for increasing economic viability of the process.

3.4 Concept of Circular Bioeconomy

Establishing a circular bioeconomy is an excellent way to reduce dependence on conventional resources and maximise the recovery of biomass waste. However, pervasive complications involved with biomass waste encompass by-products and sludge management, the diversity of waste composition, the effectiveness of processes, and the economic feasibility of scaling up and commercialising treatment technologies beyond laboratory setup (Zhu et al. 2022).

Current large-scale biomass-based energy systems face technological and economic constraints, including feedstock transportation. Apart from economic constraints, the chemical composition of feedstock also plays an important role in determining the efficacy of the system. The development and implementation of small-scale/decentralised conversion systems will aid in overcoming numerous significant challenges, including high capital costs, high complexity, and high expenses associated with feedstock. Alongside, it also ensures the consistency of biomass waste feedstock, thereby maintaining the standard of the obtained biofuel (Zhu et al. 2022). MAP is a highly scalable conversion method that is simple to establish and manage on farms. Such a dispersed biomass energy production system will give farmers additional income and fully integrate biomass feedstock producers into the bioeconomy, a crucial element in the sustainable development of renewable energy. The microwave pyrolysis of biomass is profitable when biochar, biooil, and non-condensable gases are considered (Fig. 3.3). To transform a laboratory-scale MW reactor into a MW facility suitable for commercial purposes, it is necessary to perform a technoeconomic analysis (TEA) and life cycle assessment (LCA) to evaluate the financial suitability and impacts on the environment.

3.4.1 Technoeconomic Analysis of Microwave-Assisted Processes

In order to do an accurate comparison of technologies, it is necessary to first identify the critical factors that influence the overall profitability of the product. To accomplish this, a technoeconomic assessment (TEA) shall be conducted on various production methods developed specifically for the large-scale biofuel production. The basic objective of TEA is to ascertain production costs. TEA is commonly used in the initial phase of product development to rule out less desirable options and establish performance goals for the development process (Shah et al. 2016). After a best design alternative has been chosen, a TEA is performed in detail for its building and implementation, following the steps as represented in Fig. 3.4. It provides cost

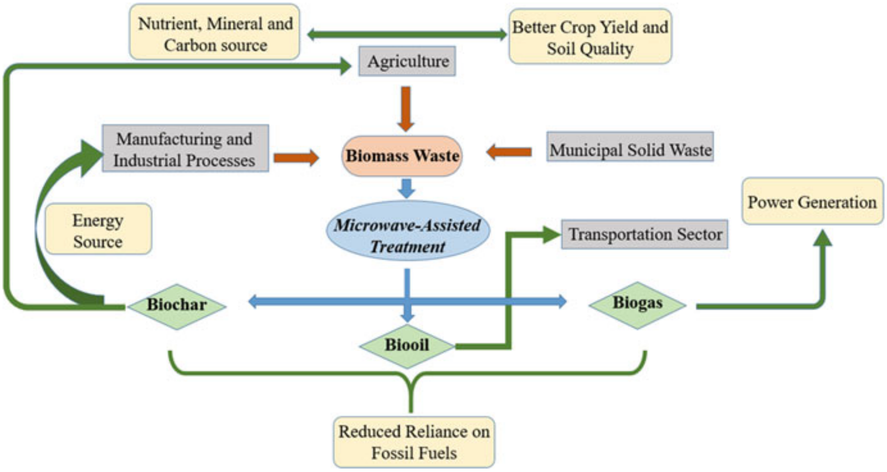
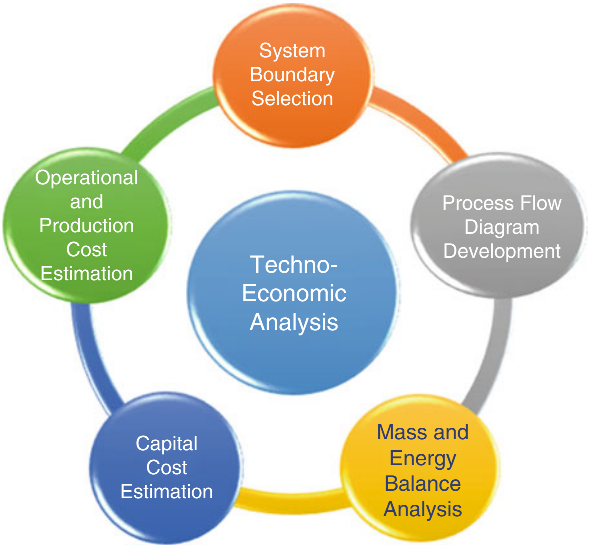


Fig. 3.3 Circular bioeconomy of MW-assisted bioenergy production

Fig. 3.4 Steps involved in technoeconomic analysis



and performance boundaries which further assist in the reduction of unnecessary costs and investment risks.

Typically, a TEA comprises of a market research (data collection and analysis) including the study of mass balance and energy balance. Further, a detailed cost estimate is conducted prior to a financial examination. Lastly, a risk and sensitivity analysis is carried out (Haeldermans et al. 2020). The TEA majorly involves capital expenditure (CapEx) and operation expenditure (OpEx) along with material processing and fabrication cost. CapEx includes costs related to purchases,

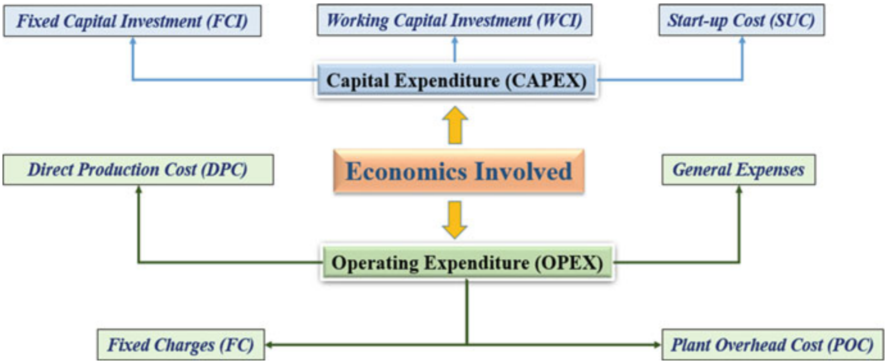


Fig. 3.5 Classification of economic aspects of TEA

installation, financing, engineering, and construction. Besides OpEx involves costs related to raw materials, energy, and labour (Fig. 3.5). Capital cost investments are calculated using an assumed market price of the operating equipment. Besides the capital and operating cost investments are evaluated based on both of the mass balance and energy balance outputs from the processing models (Wang et al. 2015b).

Major parameters that are to be considered in TEA of MW commercialisation are scale-up factors involved in total variable cost calculation, energy consumption in biomass collection and pre-treatment, energy consumption in MW process, the conversion ratio of electricity to MW and MW to dielectric heat, the energy requirement for condensation and separation of biofuels, and the energy value of the biofuel products (Lam et al. 2019). Apart from these considerations, there are certain challenges for MW commercialisation listed in Table 3.2.

It is estimated that electrical energy of approximately 1500 W is required to produce MW power corresponding to 500 W (Siddique et al. 2022). This could hinder the scaling up of MW processing techniques unless alternative arrangements are developed for the effective operation of the MW on a large scale. To address the greater energy requirement constraint in MW processes, the ignitable gases produced from biofuel production can be employed to produce electric power and thereby operate the system. The energy balance shall be helpful in the technological and financial evaluation of the MW technology for biomass processing. The overall energy valuation of the MW system is extremely important since it directly affects the effectiveness of the system as a whole. To be competitive, MW technology for biomass processing needs a sizable positive net energy balance (NEB) that can be stated as the net energy (gap/disparity between the energy content of products and input energy) per unit of mass of feedstock (Zhao et al. 2011).

At the same temperature, it is frequently stated that the biochar yield by MW pyrolysis (MWP) is lower than that produced by conventional pyrolysis (CP). Yet it is important to point out that biochar made in MWP can have improved qualities such as a greater pore volume and surface area, as well as a lower concentration of contaminants such as polycyclic aromatic hydrocarbons (PACs) in the pores

Table 3.2 Technoeconomic challenges associated with MW commercialisation (Siddique et al. 2022; Zhu et al. 2022)

Sl No.	Challenges	Problems associated
1	MW absorber and catalyst requirement	Thermal runaway effect and non-homogeneous heating effect product composition
		Difficulty in catalyst recovery
		Rapid catalyst contamination/deactivation
		Creation of local hotspots
2	Process parameters	
	(a) Temperature measurement	Accurate temperature measurement is challenging
		In the case of an ungrounded thermocouple sensor, a spark will be generated at the probe tip. Fibre optic probes are non-reactive but very expensive
		Larger the sample size, the lesser the microwave penetration depth
	(b) Sample size	As the size increases, density reduces leading to a lower heating rate
		Longer retention time reduces the biooil yield
	(c) Retention time	Difficulty in maintaining MW power in the commercial process due to larger cavity volume and biomass loading
	(d) MW power	
3	Mode of microwave processing	
	(a) Batch mode	Large commercial processing creates MW penetration depth problem leading to higher energy consumption and non-uniform heating
		Complex design
	(b) Continuous mode	Electric discharge or arcing occurs due to the moving parts inside the reactor
4	Reactor design	Cavity opening greater than the threshold wavelength induces MW leakage
		The uncovered waveguide leads to the vapour deposition inside the magnetron head
		Cleaning difficulties and reduced MW interaction due to tar deposition on the reactor walls
		Expensive quartz reactors for commercialisation

(Haeldermans et al. 2020). As a result, the value of MAP-derived biochar has the ability to escalate. This accounts for achieving the breakeven point earlier with MWP as compared to CP. Typically, sensitivity analysis is used to find the most influential elements affecting the economic benefits of certain MW processes. It can be stated that scaling up of MW to the industrial level is significantly dependent on the energy conversion efficiency of the commercial MW reactor, resultant biofuel quality and quantity, optimised process conditions, and net energy balance of the system. Zhu et al. (2022) compared the microwave-assisted catalytic pyrolysis process with conventional fast pyrolysis where the TEA study showed relatively lower capital cost involved (reduced by circa 50%) in pyrolytic conversion process into biofuel, thereby determining the potential of MACP in overall cost reduction. The minimum selling price (MSP) of the obtained biofuel shall be calculated assuming different parameters involving internal rate of return (IRR), project life, and plant operating time along with the calculated operation cost. Table 3.3 represents the MSP of different types of biofuels produced from various MW-assisted bioconversion processes.

As there exist uncertainties in both the system design data and the cost assessment data, the reliability of the results and the most influential criteria for further development can only be evaluated through a sensitivity analysis. Feedstock price and biofuel yield are the next most critical factors (Haeldermans et al. 2020). These risks can be mitigated by arranging a fixed agreement to acquire the feedstock. Research needs to focus on enhancing conversion efficiency in order to boost the financial advantage. Production of both liquid biofuel and better-quality biochar at the same time, with added value, can probably be a significant bioconversion technique for maximising environmental and economic advantages (Zhu et al. 2022).

3.4.2 Life Cycle Assessment of Microwave-Induced Techniques

Life cycle assessment (LCA) is the analysis of the environmental impact of the product throughout its lifetime. LCA aims at comparing the environmental efficiency level of the products such that the most unproblematic can be selected. The word ‘life cycle’ implies to the concept that for a valid, comprehensive evaluation of the feedstock production, fabrication, distribution, utilisation, and disposal (encompassing each and every stage of transport in between) must be evaluated. Additionally, the concept can be utilised to optimise the environmental performance of the product. LCA focuses primarily on the impact created on the environment by examining all resource and energy inputs and numerous emissions into the environment, as opposed to feasibility and profitability from a technological and economic standpoint. It typically quantifies the mass and energy exchanges between the processing system and the surrounding environment, with ‘cradle-to-grave’ boundaries involving biomass pre-treatment, bioconversion route, production stage, and end-of-life handlings like biofuel and chemical waste treatment. Yet LCA for biofuels and chemicals is normally confined to the ‘cradle-to-gate’ system boundaries of that production stage, eliminating usage, and waste management (Vignesh et al. 2022).

1. The LCA evaluation constituents of four phases/steps, having regard to the International Organization for Standardization (ISO) rules for carrying out life cycle assessment (LCA) in the ISO 14040 and 14,044 series, are Defining scope and goal

Table 3.3 Calculated MSP of biofuels from different MW processes

Feedstock	Process	Scale	Yield (wt%)	Product	Project life (Years)	IRR (%)	MSP	References
Forest residue	MACP	2000 dry tonnes/day	Biochar—28%	Upgraded biofuel	10	10	$1.02/L	Zhu et al. (2022)
			Biooil—36%					
			Upgraded biooil—65%		20		$0.97/L	
Lignocellulosic biomass	Hydrogenation using *n*-hexane	1000 dry tonnes/day	Jet fuel—0.182 mL/day	Jet fuel	20	–	$1–1.26/L	Yang et al. (2018)
			Biochar—0.958%					
Douglas fir wood pellets	MAECP	Small scale	Biooil—35%	Biofuel	–	–	Biooil—$0.66/L	Wang et al. (2015b)
	480 °C, 700 W, 20 min		Biochar—40%				Biochar—$0.4/kg	
			Syngas—25%					
Food waste+ LDPE	MWCP	100 kg/day	Biooil—42%	Biofuel	20	7	Biochar + biooil—40INR/kg	Neha et al. (2022)
	550 °C, 15.12 min		Biochar—42%					
			Pygas—16%					

MWCP microwave co-pyrolysis, *MAECP* microwave-assisted ex situ catalytic pyrolysis, *IRR* internal rate of return, *MSP* minimum selling price, *LDPE* low-density polythene

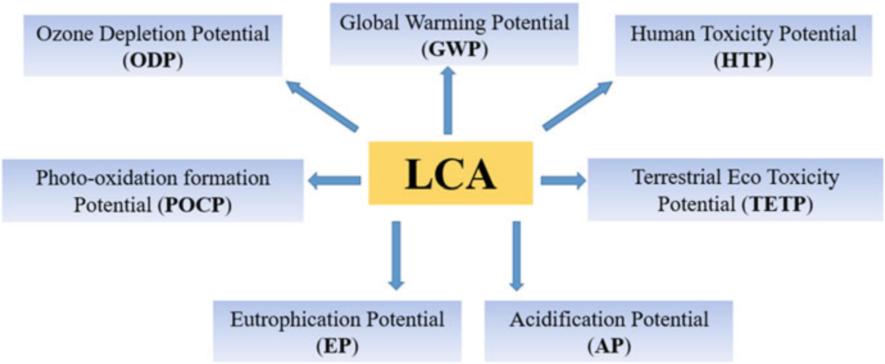


Fig. 3.6 Potential environmental impacts considered in LCA

2. Life cycle inventory (LCI) analysis
3. Life cycle impact assessment (LCIA), and
4. Life cycle interpretation.

The goal and scope of the assessment are to specify what portion of the life cycle of the product would be devoted to the evaluation and for which purpose the evaluation would serve. In this step, the standards used to evaluate different systems and specific times shall be explained. It aims to determine the environmental effects of the thermal degradation of biomass waste. The LCA analysis generally follows a cradle-to-gate methodology, within a system boundary that includes waste collection, waste treatment using MAP process, and the production of biochar, biooil, and non-condensable gases. A functional unit shall be determined during the assessment such that all emissions, energy usage, and operational expenses are determined based on the defined functional unit. In the second step, inventory analysis describes the energy and material flows inside the system boundary, focusing on its relationship with the surrounding environment, the raw materials it consumed, and environmental emissions. Every significant step and ancillary material and energy flows are subsequently detailed. LCI typically entails collection of data and estimation processes required for modelling the product system's life cycle phases. In commercial MAP units, transportation, dehumidifying, grinding, feeding, pyrolysis, and quenching of volatile matter are usually regarded as functional units. Information from inventory analysis (LCI) is used for impact evaluation (Neha et al. 2022). The impacts shall be evaluated using relevant information from the life cycle inventory database like Ecoinvent 2.0 and GaBi, as well as reports from renowned energy-related institutions (Mong et al. 2021). In the third step, the indicator results for all impact categories are detailed, and the importance of each impact category is determined through normalisation and, eventually, weighing as per the methodology articulated in ISO 14040 and ISO 14044. The potential environmental impacts considered in LCA of MW-assisted bioenergy production processes are depicted in Fig. 3.6. The final step is the interpretation of a life cycle, which includes a critical review, the determination of data sensitivity, and the presentation of the results.

Table 3.4 Stability assessment of biochar based on O/C ratio (Mohamed et al. 2022)

O/C ratio	Stability	Estimated half-life
<0.2	Most stable	>1000 years
0.2–0.6	Stable	100–1000 years
>0.6	Less stable	<100 years

CH_4, NO_x, N_2O, and CO_2 emissions are widely used to calculate the global warming potential (GWP) of MAP (kg CO_2 eq). The term 'acidification potential' (AP) refers to the discharge of acidic compounds such as hydrocarbons, SO_2, NH_3, and NH_x. These compounds have a significant negative effect on the surrounding ecosystem because they are capable of combining with other components of the atmosphere to generate acid rain, which reduces the pH of soil and water and thereby has a negative impact on biotic environment. AP is typically denoted in terms of the equivalent amount of sulphur dioxide emitted (SO_2 eq). The eutrophication potential (EP) is the increment in the supply rate of organic matter into an ecological system, denoted in the form of phosphate equivalent (${PO_4}^{-3}$ eq), considering the NO_x and NH_3 concentrations. This metric evaluates the effects of releasing excessive quantities of macronutrients into the soil, air, and water. The carbon sequestered in biochar shall be established according to the elemental constituents of the biochar. According to Mohamed et al. (2022), the O/C and H/C ratios of the char products can be utilised to predict the stability of the biochar and environmental improvement ability. It has been demonstrated that the structural stability of biochar and carbonaceous materials is determined by the relationship between oxygen and carbon (Table 3.4).

Recently, Neha et al. (2022) studied the microwave co-pyrolysis of food waste (FW) alongside LDPE extensively in terms of LCA. In this sense, the cradle-to-gate methodology was applied to the LCA evaluation in which the system boundary is comprised of certain functional elements, such as drying, transportation, shredding, pyrolysis, and quenching with the purpose of the creation of biooil, biochar, and pygas. Beyond issues that are common to all biofuel production strategies, such as soil degradation and ecosystems protection, the most frequently documented negative effect on the environment caused by pyrolysis processes is the potential for global warming, thenceforth eutrophication and acidification in terms of the equivalents of CO_2, ${PO_4}^{-3}$, and SO_2, respectively (Table 5). Considering 100 kg of feedstock as the functional unit (FU), the GWP was evaluated to be 38.92×10^3 g CO_2 eq/FU, EP and AP were reported to be 7.7 g ${PO_4}^{-3}$ eq/FU and 48 g SO_2 eq/FU, respectively, for the commingled FW with LDPE microwave co-pyrolysis which is significantly less than open dumping (420 kg-CO_2 eq.) and the landfill (200-kg CO_2 eq) of FW (Neha et al. 2022). Similar environmental impact studies of other feedstocks for bioenergy production are listed in Table 3.5. Commercial MW pyrolysis plant life cycle assessment data revealed that drying and MW pyrolysis reactors accounted for around 90% of energy consumed and contributed majorly for the impacts on environment (Neha et al. 2022; Mong et al. 2021). Several practical arguments include (a) enhancing biooil to efficient biofuels, (b) biochar upgradation to activated carbon, and (c) utilisation of syngas for power production to develop the

Table 3.5 Environmental impacts in terms of GWP, EP, and AP (per FU)

Feedstock	Process involved	Catalyst	System boundary model	FU	GWP (kg CO_2 eq)	EP (kg PO_4^{-3} eq)	AP (kg SO_2 eq)	References
Switchgrass	MWCP	K_3PO_4	Cradle to gate	1 ton of feedstock	$1.93*10^2$	$2.52*10^{-2}$	$1.3*10^{-1}$	Mohamed et al. (2022)
Switchgrass	MWCP	SiC	Cradle to gate	1 ton of feedstock	$2.23*10^2$	$4.1*10^{-2}$	$1.51*10^{-1}$	Mohamed et al. (2022)
MSW	CP	–	Cradle to gate	1 kg of organic MSW	1.25	$0.18*10^{-3}$	$2.35–10^{-3}$	Wang et al. (2015a)
Horse nanure (HM)	MW pyrolysis	Coconut shell activated aarbon	Cradle to gate	1 ton of dried HM	$2.28*10^2$	$2.39*10^{-2}$	$1.05*10^{-1}$	Mong et al. (2021)
HM	LSI	–	Cradle to gate	1 ton of dried HM	$0.6*10^2$	$0.6*10^{-2}$	$2.87*10^{-2}$	Mong et al. (2021)
Oil palm EFB	Fast pyrolysis	–	Cradle to gate	1 kg of biooil	4.46	–	–	Chan et al. (2016)
Oil palm EFB	HTL	–	Cradle to gate	1 kg of biooil	2.29	–	–	Chan et al. (2016)
Forest residue	MWCP	K_3PO_4	Cradle to gate	1 MJ of biofuel	$-57.3*10^{-3}$	–	–	Zhu et al. (2022)
FW+ LDPE	MW co-pyrolysis	GAC	Cradle to gate	100 kg of feedstock	38.92	$0.77*10^{-2}$	$4.8*10^{-2}$	Neha et al. (2022)

MWCP microwave catalytic pyrolysis, *MSW* municipal solid waste, *CP* conventional pyrolysis, *LSI* large-scale incineration, *HTL* hydrothermal liquefaction self-reliability of MAP of biomass waste. Polycyclic aromatic hydrocarbons are toxic and carcinogenic organic pollutants resulting from the incomplete combustion of organic matter. Reducing the amount of polycyclic aromatic hydrocarbons in biooil shall reduce its toxicity. There are various types of catalysts used for distinct outcome enhancements. Certain catalysts for MAP of biomass have a greater selectivity for converting aliphatic hydrocarbons to aromatic and cyclic compounds alongside decreasing the oxygenate concentration like acids, aldehydes, ketones, and carbonyl. Metallic materials (e.g. oxides, salts, zeolites) have a greater thermal conductivity and therefore serve as microwave absorbers and catalysts to accelerate pyrolysis reactions (Ge et al. 2021).

Microwave-induced pyrolysis of horse manure has a lower environmental impact than conventional pyrolysis of swine manure due to reduced energy utilisation and higher conversion efficiency. Manure valorisation via pyrolysis produces three components of end products (biochar, biooil, and syngas) that can be utilised as biofuel and organic chemicals, thereby decreasing the carbon release into atmosphere while simultaneously treating the manure. Additionally, the LCA study demonstrates that microwave-assisted pyrolysis is a promising animal waste treatment process which can pertain to the sustainability objective of GWP and other environmental impacts of minimisation (Mong et al. 2021).

3.5 Conclusion

The abundant availability of biomass waste sources like agricultural waste across the country provides a better opportunity to utilise them for converting into energy sources. Microwave pyrolysis is one of the potential sustainable energy generating technologies since it can convert agricultural waste into renewable and novel biofuels like biochar, biooil, and syngas in comparatively lesser time but improves its quality as well. The availability of this technology in commercial scale is still in infancy. There is limited data available based on LCA studies of commercial/pilot scale MW-assisted bioenergy production processes. Yet, on the basis of technoeconomic and environmental assessments, it can be determined that MW pyrolysis technology is both economically viable and environment friendly. The availability in abundance and sustainable supply of biomass feedstock encourages the concept of transforming waste biomass into sustainable biofuels, an innovative and potentially lucrative form of unconventional energy generation strategy to efficiently combat the energy crisis.

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4 Biochemical Approach for Transformation of Agricultural Waste to Bioenergy and Other Value-Added Products Through the Bioelectrochemical System

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Abstract

Agricultural industries are the largest waste producer that comprises a major problem worldwide due to the adverse effect of agro-waste on the environment, economy, and social life. Annually 1300 million tons of trash are produced from the agricultural fields, out of which up to 50% are raw materials dumped without treatment. Therefore, minimising agricultural solid waste is imperative to combat its detrimental effects on the health of humans and other animals. Furthermore, agro-waste contains different bioactive compounds such as lignin, cellulose, chitin, and polyphenolic compounds; therefore, it can be envisaged as a potential source for producing biofertiliser, biofuel, biogas, enzymes, vitamins, antioxidants, and other value-added products. Additionally, utilising agro-waste as a raw material diminishes production costs and provides the scope of additional revenue for the reliant industries. Also, the synchronised recovery of renewable energy and wastewater treatment through bioelectrochemical systems (BES) utilising agro-waste products as feedstock demonstrates a waste biorefinery approach leading towards a sustainable circular bioeconomy. Therefore, this chapter elucidates the application of different agro-waste products in the field

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of BES and their effects on bioenergy production and other value-added product recoveries. Moreover, this chapter aims to enlighten the readers on the advancements in biochemical processes for agro-waste remediation and biochemical conversion technologies to recover valuable biochemicals. In addition, different roadblocks associated with biochemical conversion technologies, considering recommendations and future perspectives, are also highlighted. Additionally, recent developments in potential imminent research areas of agro-waste-assisted BES have also been covered to make this nascent technology ready for large-scale implementation.

Keywords

Agro-waste · Bioactive compounds · Biochemical conversion · Value-added products · Bioelectrochemical system

4.1 Introduction

The scarcity of energy is a continually growing global worry that has been spurred on by an increase in population, rapid industrialisation, and engineering advancements (Ghasemi et al. 2013). Moreover, the excessive consumption of nonrenewable energy sources, such as coal, petroleum, other crude oil, and natural gas, to meet the rising global energy demand of the population worldwide is another major concern that could trigger an energy crisis in the near future (Ahmad and Zhang 2020). In addition to the exhaustion of fossil fuels and associated detrimental impacts on ecological systems, the open disposal of agro-waste in developed and underdeveloped nations significantly contributes to environmental spoilage, which is another significant worldwide issue. In order to conquer the dilemma of the global energy crisis and lessen associated environmental risks, scientists are striving towards using eco-friendly and renewable energy sources (Kabeyi et al. 2022). Therefore, recuperating bioelectricity and other gaseous and liquid biofuels from a variety of agro-waste may suggest a renewable economic explanation that opens the possibility of fulfilling the global energy demand.

Increased global population, urbanisation, economic expansion, and shifting production and consumption patterns contribute to the abundance of bio-waste generation. Specifically, agricultural bio-waste, a typical renewable energy source with plenty of nutrients and easily biodegradable organic materials, are obtained from various biological sources and industrial processes. These waste products can be decomposed easily under both aerobic and anaerobic conditions. One of the most prevalent techniques for recovering resources from trash is anaerobic digestion, which converts organic waste into biogas, while leaving behind additional resources like value-added nutrients (Kamperidou and Terzopoulou 2021). Moreover, starch, cellulose, protein, hemicellulose, and lipids are the key components of these bio-wastes, and they can be used as inexpensive raw materials to generate value-added products. However, further treatment should be required to treat xenobiotic compounds, heavy metals, and other contaminants prior to disposal in the ecosystem. Therefore, a distinct approach is obligatory to recover the bioenergy while remediating the primary pollutants in wastewater. Thus, recovery of power along with other biofuels through a single bioelectrochemical system (BES) using agro-waste as the substrate may propose a renewable, economical elucidation for the circular bio-economy.

In this veneration, BES provides an enormous opportunity for synthesising renewable bioenergy and other valuables while simultaneously purifying wastewater (Ghangrekar et al. 2022). The organic material in wastewater can be metabolised by exoelectrogens and generate protons, electrons, and CO_2. While electrons are transferred through the external circuit connected between the anode and the cathode of a BES, where they are typically combined with oxygen to produce H_2O with the reaction of protons released in bulk anolyte that migrate towards the cathode through the proton exchange membrane (PEM). In the case of a microbial fuel cell (MFC), biochemical energy is converted to electrical energy during the flow of electrons from the anode to cathode via an external circuit. On the other side, external power is provided to endorse the H_2 generation through microbial electrolysis cell (MEC) (Koul et al. 2022).

The cutting-edge BES technology has the capacity to produce valuable chemicals while simultaneously producing sustainable and renewable energy using wastewater as substrate. In 1911, Potter initially developed a galvanic cell utilising platinum as the cathode for power generation via cultivating two exoelectrogens such as *Saccharomyces cerevisiae* and *Escherichia coli* (Potter 1911). This widened the door for further research that centred not only on bioenergy production and wastewater treatment rather also on resource recovery from different wastewater. For improved power generation and pollution removal, hybrid systems such as membrane bioreactors have also been combined with MFC (Bhowmick et al. 2019). One such effort combines an MFC with an agro-waste-derived membrane bioreactor to handle medium-strength effluent (Bhowmick et al. 2019). Nevertheless, the difficulties and expenses related to the fabrication of reactors and cultivation of exoelectrogens might hinder its widespread application on a real-scale.

For the utilisation of inexpensive components in MFC systems to weaken the overall cost, waste-derived biomass may offer an intriguing alternative to expensive electrocatalysts. Therefore, this chapter focuses on agricultural waste and the techniques used to turn it into valuables including bioenergy in terms of liquid and gaseous biofuel, enzymes, antibiotics, ethanol, and single-cell proteins. In light of this, employing agro-biomass waste, such as food, sludge, and forestry wastes, is a tempting initiative of commercialising BES. Furthermore, the environmental and health risks associated with BES during wastewater treatment and bioenergy recovery can be significantly decreased by using waste biomass resources as energy sources.

The potential use of biomass waste as a substrate for different BES has been confirmed by a number of preceding research, including those on algal biomass, and lignocellulosic biomass and agro-based wastewater or effluents (Sani et al. 2021; Ali et al. 2020; Wang et al. 2021). Further, Chakraborty et al. (2020) developed a low-cost biochar-derived PEM by pyrolysing food waste at 600 °C and achieved 81% of chemical oxygen demand (COD) removal efficiency from the MFC fabricated with this membrane (Chakraborty et al. 2020). The same research group also elucidated the economic sustainability of this biochar, which had a maximum power yield per unit cost of PEM that was 26-folds greater (0.278 W/$) than Nafion 117 (0.011 W/$) (Chakraborty et al. 2020).

Additionally, different agro-waste effluents served as the substrate for exoelectrogens in MFC to enhance the system's performance. For instance, palm oil mill effluent inoculated with anaerobic sludge has been treated in a single chamber MFC and achieved a maximum of 304 mW m^{-2} of power density along with 45% of COD removal efficiency (Baranitharan et al. 2015). Furthermore, hydrolysate formed after converting the solid residue present in agro-waste like rice husk, wheat straw, and corn stover into carbohydrate-rich fermented products during solid or semisolid-state fermentation can also be utilised as a substrate in MFC (Schievano et al. 2016). Therefore, this chapter devoted an effort to thoroughly evaluate the sources and varieties of agro-waste, management issues, and a wide variety of agro-waste treatment technologies to turn bio-waste into bioenergy. Also, the prospective advantages of transforming agro-waste into value-added products through BES and future recommendations for the commercialisation of this technology are overviewed. Thus, the utilisation of green and inexpensive agro-waste in BES enables an inventive strategy of concurrent wastewater treatment along with resource recovery, thus demonstrating the concept of the circular bio-economy.

4.2 Agro-Waste Sources as Raw Material

Agricultural wastes or agro-wastes are crop residues and/or first processed raw agricultural products such as fruits, vegetables, dairy products, poultry, meat, and other products (Obi et al. 2016). Generally, agro-waste is generated during agricultural activities such as farming, horticulture, nursery plots, seed production, market gardens, dairy livestock breeding, grazing, and forestry or woodland production (Lim and Matu 2015). Moreover, agro-wastes can be classified as solid, liquid, or slurry depending on their physical state and be generically categorised into crop residues, agro-industry wastes, livestock wastes, and fruit and vegetable wastes (Fig. 4.1).

According to grain-to-residue conversion factors and grain production data, crop residue production has more than tripled from 1589 million tons (Mt) in 1960–1961 to 5280 Mt in 2020–2021 (Shinde et al. 2022). Hence, it is necessary to utilise these massive pools of unused resources that can be transformed into valuable assets with multiple beneficial industrial applications. Crop residual wastes left on crop-cultivated land, including leaves, stoners, straws, seed pods, etc., are the most abundant organic wastes that can be easily transformed into value-added products. The agro-waste such as rice straw, wheat straw, corn stover, etc. are extensively utilised to produce ethanol and other value-added liquid fuel. However, many other crop residues including rotten fruits and vegetable at the cultivation farm can be used

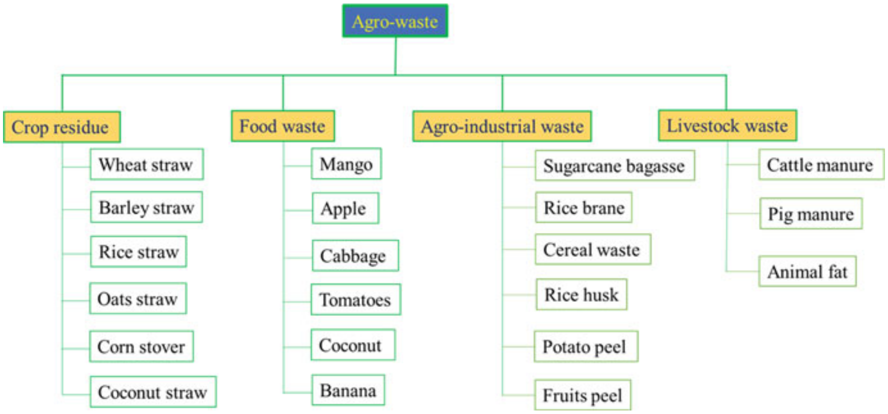

Fig. 4.1 Classification of agro-waste derived from natural and environmental sources

to recover other valuable products such as biochar, biogas, fertiliser, secondary metabolites, antioxidants, and so on.

Agro-industrial waste management provides multidimensional output in the form of valuable product recovery and also retardates its harmful impact on the environment and human and animal health. Moreover, due to some of the constituents in agro-industrial waste, it has gained much attention as a raw material for different sustainable products and bioenergy production (Beltrán-Ramírez et al. 2019). With an estimated annual bagasse production of 180.73 Mt worldwide, sugarcane bagasse, a lignocellulosic waste, is the major contributor to agro-industrial waste (Pattanaik et al. 2019). Different agro-industrial residues, such as waste products from the food, alcoholic, and vegetable and fruit peels, and fruit pomace after extraction of juice are extensively utilised for the production of enzymes and other valuables. In addition to starch residue derived from starch-manufacturing industries, various other by-products such as sugarcane bagasse, molasses from sugar manufacturing industries, de-oiled seed cake from edible oil manufacturing industries, chicken skin, egg, meat, and animal fat from slaughterhouses and meat processing industries have been found to have a noteworthy impact on the production of diverse value-added products (Lopes and Ligabue-Braun 2021). Other major contributors of agro-industrial waste are waste from the palm oil industry, apple pomace, orange peel, and some nonfood-based waste such as de-oiled seed cake of nonedible oil from *Jatropha curcas* and *Pongamia pinnata*.

Livestock is another foremost agro-waste source, which are classified as liquid manure (urinary waste), solid manure (farmyard manure), and other industrial or municipal wastewater generated. Livestock-based waste includes manure and organic materials in the slaughterhouse, wastewater from the bathing of animals, and maintaining sanitation in slaughterhouses. The annual livestock waste generation in India is about 3 Mt (Kumari and Dhawal 2020). As most livestock farms are built near or in the residential area, air pollutants such as H_2S and CH_4 and odours from livestock waste are serious concerns; therefore, proper waste management is required to alleviate this issue. A prevalent greenhouse gas, CH_4, accounts for roughly 30% of global anthropogenic greenhouse gas emissions; however, animal wastes alone account for 32% of global CH_4 emissions, which are also responsible for significant energy loss (Kimothi et al. 2020). According to the Indian Council of Agricultural Research's, New Delhi, report, the annual energy loss of 38×10^8 Giga calories was estimated from livestock waste CH_4 emissions (Kimothi et al. 2020). Using cutting-edge scientific technology, livestock waste can be recycled to combat rising energy prices, promote sustainable agriculture, and mitigate environmental threats. Moreover, livestock is an essential component of the agricultural circular bioeconomy, converting non-edible biomass into high-quality food and recycling large amounts of nutrients to the agroecological system via farmyard manure.

4.3 Applications of Different Agro-Waste Materials

Utilising agro-wastes as raw materials can be an optimistic approach to subordinate production costs as well as environmental pollution (Sadh et al. 2018). The lignocellulosic agro-industrial residues usually have high concentrations of glucose, xylose, mannose, arabinose, and other organic compounds that can be anaerobically oxidised to produce bioethanol and valuable biogas. On the other hand, lipid-containing agro-waste is considered as a potential feedstock for biodiesel and biogas production. Moreover, agro-waste is a rich source of bioactive compounds that further add to its applications for real life in recovering fertiliser, plant secondary metabolites, antibiotics, and other valuable products.

4.3.1 Production of Bioenergy from Different Agro-Waste

The agro-waste rich in fermentable cellulose, such as sugarcane molasses, sugarcane bagasse, and corn stalk, produces ethanol and biogas. In contrast, lipid-rich agro-waste, such as nonproductive oil seeds, is a feedstock for biodiesel production (Donzella et al. 2022). Moreover, bioenergy production depends on the types of agro-waste; in this regard, anaerobic digestion of 74 manures and 78 crop straw resulted in the bio-methane production of 335.5–620.4 STP mL g^{-1} VS for manures and 434.0–540.3 STP mL g^{-1} VS for crop straws (Wang et al. 2019). Similarly, a comparative ethanol recovery from yeast culture on lignocellulosic agro-waste such as sugarcane bagasse, rice straw, corncob, and sweet sorghum bagasse was investigated by Nunta et al. (2023). The investigation revealed that fungal strain *Candida tropicalis* cultivated with rice straw generated maximum 15.3 g L^{-1} of ethanol after 24 h of cultivation (Nunta et al. 2023). Operating parameters also affect biofuel yield; for instance, at optimal 92.59 °C hydrolysis temperature, 30 min operation time, and 1% acid concentration, Berhe and Sahu achieved a maximal yield of 10.86 mL ethanol per 50 g of sugarcane bagasse biomass (Berhe and Sahu 2017). Moreover, Donzella et al. (2022) recovered 55% of lipids from pumpkin peel through yeast fermentation by cultivating oleaginous yeasts *Rhodosporidiobolus azoricus* and *Cutaneotrichosporon oleaginosum* (Donzella et al. 2022).

Hydrogen is considered the most suitable alternative future fuel for transport and other sectors (National green hydrogen mission GOI). Zhang et al. (2020) investigated the biohydrogen production from cornstalk; a maximum of 424.3 mL H_2 g^{-1} of cornstalk was reported at two-stage fermentation (dark fermentation followed by photo-fermentation) in this investigation (Zhang et al. 2020). In another investigation of biohydrogen production from thermochemically pretreated corncob using a mixed culture bio-enhanced with *Clostridium acetobutylicum*, a maximal biohydrogen yield of 132 L kg^{-1} of corncob biomass was reported (Medina-Morales et al. 2021). Therefore, the application of different agro-wastes for both liquid and gaseous fuel productions can be a promising carbon neutral revelation, which would alleviate the nuisance of global warming and energy crisis.

4.3.2 Other Biochemicals' Recovery

Agro-waste is one of the most cost-effective substrates for extracting biochemicals of commercial value, such as microbial pigments, fragrance compounds, antioxidants, antibiotics, and plant growth hormones. Utilising agro-waste as feed-stock for biochemical synthesis reduces environmental and health risks, while simultaneously enhancing the economic value of the bioprocess. For instance, orange peel is an agro-waste that generates enormous quantities and it is a source of natural pigments such as carotenoids; for example, the carotenoids yield of 97.4 ± 17.1 μg g^{-1} of dry biomass (orange peel) was reported in an investigation (Murador et al. 2019). Similarly, anthocyanins have multiple health benefits, and their extraction from food waste has recently become a topic of interest (Diaconeasa et al. 2022).

Cutin and suberin are biopolymers made from fatty acids and aromatic compounds. Cutin is the primary component of the cuticle, which is the waxy, water-repellent outermost layer of exposed cell walls. Few approaches have been recently discovered to extract cutin monomers from various agro-wastes on an industrial scale (Heredia-Guerrero et al. 2017). Agro-waste also contains many bioactive compounds such as polyphenols, tannins, flavonoids, vitamins, essential minerals, fatty acids, volatiles, anthocyanins, pigments, bioactive peptides, whey, and colostrum (Ben-Othman et al. 2020). Asagbra et al. (2005) investigated the presence of antibiotics in agro-waste in which peanut shells were identified as the most productive substrate for tetracycline (4.36 mg g^{-1}), followed by corncobs (Asagbra et al. 2005). Therefore, agro-waste is a plausible source for pharmaceuticals and other nutrients and minerals, rendering it a feasible option that will aid in fulfilling the increasing demand for nutrients in the health sector.

Biochar is a carbon-rich material produced by incomplete combustion of biological material such as agro-waste in the absence or with a limited amount of oxygen (Susilawati et al. 2020). Conversion of agro-waste to biochar is one of the most sustainable approaches for carbon sequestration and soil amendment agent.

Soil fertility degradation and nutrient depletion are common threats to agroecosystems, posing a challenge for modern agricultural practices aimed at balancing soil fertility factors (Pradhan et al. 2020). In this regard, agro-biochar has recently gained adequate interest due to its agronomic applications. Biochar derived from agricultural sources is utilised as a soil amendment to enhance the physical and chemical properties of soil, thereby augmenting the soil's nutrient accessibility and water retention potential. Furthermore, the burial of biochar in soil results in a gradual decomposition process, thereby functioning as a durable carbon reservoir. Additionally, biochar also influences soil microbiology and enzyme activity, which helps to enhance plant growth and crop yield (Enaime and Lübken 2021).

A recent investigation demonstrated that applying agro-biochar as fertiliser enhances crop growth; however, its combination with mineral fertiliser could improve its physiological attributes regarding chlorophyll fluorescence indicators (Mustafa et al. 2022). Moreover, due to their structure, agro-biochar can have diverse applications, such as electrode material for fuel cells, supercapacitors, and batteries, and feedstock of activated carbon and carbon nano-filaments (Wahi et al. 2015; Khedulkar et al. 2023). Agro-biochar is also considered a clean and alternative energy source of fossil fuels. The biochar yield depends on the parameters such as pyrolysis temperature, biomass, and pyrolysis time; the biochar from vegetable waste (cauliflower, cabbage, banana peels, and corn cob residues) showed a yield of 20–30% at the pyrolysis temperature range of 300–500 °C (Pradhan et al. 2020).

Applying agro-waste as fertiliser is an economic practice in terms of saving the cost required for chemical fertiliser. A biochar's carbon content H/C ratio is a significant property for its utilisation; stable carbon content, low H/C ratio, and high surface area and pore volume are desired for its high quality as fertiliser. In this regard, when cassava rhizomes, cassava stems, and corncobs were used for biochar production, the chemical analysis showed that corncobs yielded the highest C (81.35%) and H (2.42%) content with high surface area (Wijitkosum and Jiwnok 2019). In addition, organic fertiliser obtained from agro-waste improves soil fertility by enhancing soil aggregation, hydraulic conductivity, water-holding capacity, degree of compaction, bulk density, and resistance to wind and water erosion. Thus, it concluded that agro-waste could be the economical and sustainable feedstock for bioenergy production, fertiliser production, biochemical production, and other valuables and so on.

4.4 Traditional Agro-Waste Conversion Technologies

4.4.1 Biochemical Conversion

4.4.1.1 Anaerobic Digestion

The primary feature of agro-waste is its high organic content, which makes it useful for energy recovery and other value-added biochemicals' generation through anaerobic digestion. Anaerobic digestion is a complicated biological process in which

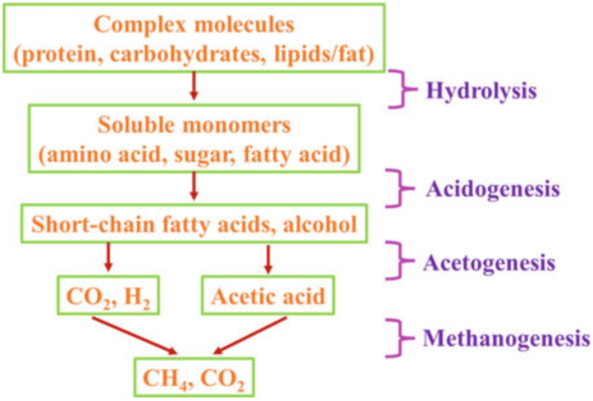

Fig. 4.2 Metabolic pathways of anaerobic digestion of biomass

anaerobic bacteria decompose organic material in the absence of oxygen. The anaerobic digestion of organic waste follows broadly four-step fermentation pathways, hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as shown in Fig. 4.2.

The main valuable products derived from the anaerobic digestion of agro-waste are biogas (CH_4 and CO_2) and digestate. During anaerobic digestion, the nitrogen in the protein is mineralised into ammonium, and the total P and K are also retained in the digestate (Schievano et al. 2011). Due to the presence of these nutrients in the digestate, it is applied to agricultural land as fertiliser. On the other hand, biogas is used primarily as fuel for heating and lighting purposes; however, it can be further transformed into alcohol or syngas (Riya et al. 2021). Biogas generated in anaerobic digesters is composed of methane (50–80%), carbon dioxide (20–50%), and between 0.2% and 0.4% hydrogen sulphide (highly toxic gas). However, the proportion of these gases in biogas is dependent on feedstock and process management (Demirbas and Ozturk 2005). Generally, the heating value of the biogas produced is in the range of 18–25 MJ m^{-3} depending on methane content (Demirbas and Ozturk 2005). The storage of biogas is impracticable due to its poor calorific value and corrosive nature. However, the benefits significantly exceed the aforementioned drawbacks. Anaerobic digestion makes it possible to handle and dispose of vast amounts of poultry, swine, and dairy waste, minimising the odour issue. This process also stabilises the waste, and the digested sludge is relatively odourless while retaining its original fertiliser value.

4.4.1.2 Fermentation

Fermentation is a biological process frequently promoted by the microorganism-derived release of enzymes that convert simple sugars into low molecular weight compounds such as alcohols and acids. The fermentation of two of the most prevalent sugars follows the two processes as shown below in Eqs. (4.1) and (4.2) (Garba 2021):

$$\text{Glucose fermentation}: C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2 \tag{4.1}$$

$$\text{Fructose fermentation}: 3C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5CO_2 \tag{4.2}$$

During fermentation, fermentable cellulosic biomass, such as sugarcane molasses, sugarcane bagasse, and corn stalk, could be converted into alcohol through biochemical pathways (Garba 2021). These pathways involve many patterns in which hydrolysis and fermentation processes are conducted in the same or different reactors, such as separate hydrolysis and fermentation, simultaneous saccharification and fermentation, and consolidated bioprocessing.

The fermentation of banana waste under the optimum condition of 60 °C temperature, pH of 7.5, 5% of inoculums size, and 5 days of incubation time, a maximum ethanol yield of 0.41 g g^{-1} of substrate was obtained on co-culturing ethanologenic *Clostridium thermocellum* CT2 with *Clostridium thermosaccharolyticum* HG8 on alkali-treated banana waste (Harish et al. 2010). In an investigation, a maximum of 249 mg gds^{-1}L-lactic acid was obtained after 5 days of solid-state fermentation (SSF) of cassava bagasse and sugarcane bagasse under the optimised conditions with a conversion efficiency of about 99% of the initial reducing sugars (John et al. 2006).

In addition to alcohol and acid production, SSF by utilising agro-waste produces enzymes, vitamins, antioxidants, animal feed, antibiotics, and other compounds (Sadh et al. 2018), for instance, the extraction of pullulanase enzyme from agro-waste using SSF (Kumar et al. 2022). Another example is laccase production with the utilisation of agro-waste substrates in SSF processes (Ghosh and Ghosh 2018). The most difficult aspect of converting agro-waste into fermentable sugars, such as hexose and pentose, is balancing the synthesis of inhibitors and desirable products. To avoid inhibitors' production and optimise hexoses' and pentoses' synthesis, microbial metabolism in the breakdown and saccharification of the biomass could be taken into account.

4.4.2 Thermochemical Conversion

The major thermochemical conversion of agro-waste to heat, biochar, biogas, and liquid fuels (bio-crude) are combustion, pyrolysis, gasification, and liquefaction. Among these thermochemical conversions, combustion is the most frequently practised for heat and electricity generation methods.

4.4.2.1 Direct Combustion

One of the oldest methods of biomass conversion is the burning of agricultural waste for the generation of fuel. Even today, it is a relatively popular practice to burn agricultural trash through stoves and pot fires for cooking and heating purpose. Lignin-rich biomass is preferred for combustion (Yan et al. 2019); however, compared to other biomass conversion processes, the process is somewhat less selective for biomass feedstock. The combustion of agro-waste-based feedstock is converted mainly to heat, CO_2, water, and a smaller quantity of other compounds depending on the composition of biomass and process parameters. The agro-waste contains more ash-forming minerals along with C, H, and O (Saxena et al. 2009; McKendry 2002). Agro-waste has more oxygenated compounds compared to traditional fossil fuels, owing to the carbohydrate content of biomass, in which dry biomass typically includes 30–40% of O_2 (McKendry 2002). During the combustion of agro-waste-based biomass, a portion of the needed O_2 is supplied by the bound O_2 in the biomass, while the remaining oxygen is provided via air injection. Combustion remains the leading method for converting agricultural waste to energy or fuels, accounting for about 95% of all biomass energy used today (Obi et al. 2016).

The practice of crop cultivation necessitates the use of chemical fertilisers and other chemical compounds that are subsequently incorporated into the biomass. Additionally, the direct combustion of residual agro-waste from crop cultivation has been found to have significant negative health consequences, including but not limited to blurred vision, bronchial infection, dizziness, asthma, and fatigue. Moreover, the process of directly combusting agro-waste lacks control in terms of energy extraction, resulting in a significant amount of energy being lost to the atmosphere. This uncontrolled process also contributes to negative environmental effects, including local heat waves and greenhouse gas emissions; hence, direct combustion method of agro-waste conversion should be avoided.

4.4.2.2 Pyrolysis

Pyrolysis, an endothermic process, is the thermal depolymerisation of organic biomass in the absence of O_2 or the presence of inert gas such as N_2 in a closed chamber at a temperature range of 300–900 °C to produce biochar, liquid biofuel, and bio-gases (Fig. 4.3) (Prasad et al. 2023). The pyrolysis yield depends on temperature, moisture content, biomass composition, particle size, and heating rate. Hence, optimising pyrolysis conditions is essential for individual and mixed biomass for the recovery of valuables.

Though pyrolysis is a well-accepted economical method for agro-waste valorisation, it has limitations in producing pyro-oil with low hydrocarbon content with lower aromatic compounds. Co-pyrolysis and catalytic pyrolysis are practised these days to overcome the limitation associated with the yield produced. Co-pyrolysis entails the incorporation of two or more distinct biomass or polymeric feedstocks. The co-pyrolysis of cow manure and stems of the weed *Amaranthus retroflexus* L. were investigated in the ratio of 1:1, 2:1, and 4:1 at a heating rate of 10 °C min^{-1} in the temperature range from 40 °C to 1000 °C. The maximum yield composition including 36.95% of pyrolysis liquid, 24.99% of syngas, and 38.06% of

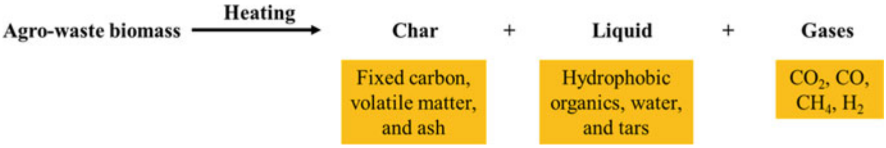

Fig. 4.3 Pyrolysis of agro-waste and the product formed

biochar was achieved through this co-pyrolysis method, whereas a maximum hydrogen concentration of 21.17% in the pyrolysis gas was reported with a 12.10% increased hydrogen output in 4:1 ratio as compared to 1:1 (Karaeva et al. 2022). The presence of a catalyst in pyrolysis influences the decomposition behaviour of agro-waste biomass as well as the composition and quality of pyrolysis yield. For instance, synthetic zeolite (ZSM-5) was shown to be useful for enhancing the deoxygenated aromatic content of pyrolysis products without decreasing liquid output (Kabakcı and Hacıbektaşoğlu 2017).

Thus, pyrolysis has been recognised as a viable option for the disposal of agro-waste as it can convert this biomass asset into granular charcoal, non-condensable gases, and pyrolysis oils, which, due to their high calorific value, can be used to produce valuable energy and chemical products (Trninić et al. 2016). However, a better comprehension of pyrolysis mechanisms is necessary for the development of thermochemical processes.

4.4.2.3 Gasification

Gasification is a commercial process that may turn any carbon-containing substance, such as coal, petroleum coke (petcoke), metallurgical coke (metcoke), or agro-waste biomass, into synthesis gas (syngas). The gasification process involves the thermochemical conversion of biomass at high temperatures (500–1400 °C), air pressures (up to 33 bar), and a low/absent oxygen concentration into a mixture of flammable gas (Biagini et al. 2014). Compared to combustion and pyrolysis, biomass gasification can recover more energy and a greater heat capacity (Lee et al. 2019). Conversion of carbon monoxide and hydrogen by pyrolysis and liquefaction is low, owing to the intricacy of these processes, which are highly dependent on operating conditions and the existence of secondary reactions caused by solid particles and volatiles. The easy catalytic methanation of carbon monoxide and carbon dioxide from syngas to synthetic natural gas is an additional advantage of the gasification process. Consequently, gasification is regarded as the optimal method of agro-waste valorisation and bioenergy production.

4.4.2.4 Liquefaction

Agro-waste-based biomass may be converted into bio-oil or bio-crude via liquefaction and pyrolysis. Thermochemical liquefaction entails the production of bio-oil at low temperatures and elevated pressure, irrespective of the use of a catalyst and in the presence of hydrogen. Hydrothermal liquefaction (HTL), also known as hydrous pyrolysis, is a well-established technique that converts biomass into bio-oil using subcritical water (SCW) at temperatures 250–374 °C and pressures range of 40 to 220 bar. In the HTL process, high pressure helps to keep water in a liquid condition; on the other hand, the combination of raised pressure and temperature decreases the dielectric constant and density, which makes hydrocarbons water-soluble. Characteristically, the HTL process employs biomass with a high moisture content to reduce the drying or dewatering step expense. In this regard, agro-waste as feedstock for liquefaction with adjustable moisture content could be a more sustainable approach for bio-oil production.

4.5 Agro-Waste Conversion Through Bioelectrochemical Systems

Bioelectrochemical systems are protuberant technology that serve the multi-faceted applications such as wastewater treatment, energy recovery, and synthesis of value-added products. Usually, BESs are categorised in accordance to biomass utilisation for value-added products' recovery (Fig. 4.4). For example, MFC utilises the biomass and generates electricity by exploitation of electroactive bacteria, whereas microbial desalination cell (MDC) can transform the chemical energy into electrical energy by cultivating electroactive microbes along with concomitant desalination of brine water. However, the energy generation during the anodic degradation cannot overcome the thermodynamic limitation of the synthesis reactions like hydrogen (H_2) and volatile fatty acid (VFA) production. To overcome this issue, H_2 gas can be synthesised in microbial electrolysis cell (MEC) through cathodic reduction of proton at abiotic cathodes by applying external voltage, while bio-cathodic reduction in the microbial electrosynthesis (MES) produces the short-chain volatile fatty acids, H_2, acidic acid, and other compounds by reduction of CO_2 and proton. For example, acetate (52.4 mM m^{-2} day^{-1}), isobutyrate (36.2 mM m^{-2} day^{-1}), propionate (41.6 mM m^{-2} day^{-1}), 2-piperidinone (26.7 mM m^{-2} day^{-1}), and traces of methyl derivatives of these compounds were recovered through MES (Das and Ghangrekar 2018).

Agro-waste, such as wheat straw, rice straw, sugarcane bagasse, corn stover, and manure, is an economical and the most abundantly available carbon source and can be utilised for generating renewable electricity and other value-added products through the BES. Investigations related to treating lignocellulosic agro-waste by-products using MFC are extremely limited due to the recalcitrant nature of lignin and cellulosic matter. However, some investigations described the utilisation of hydrolysate obtained from the expulsion, pyrolysis, and acidic/enzymatic treatment of agro-waste for better power output in MFC (Fig. 4.4). For instance, a single-

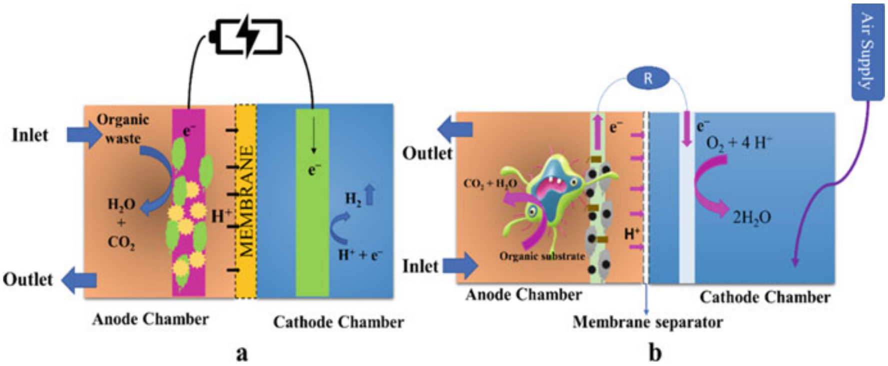

Fig. 4.4 Schematic representation of (**a**) microbial electrolysis cell and (**b**) microbial fuel cell for the production of bioelectricity and bio-hydrogen

chambered MFC supplied with the rice straw hydrolysate having initial COD of 400 mg L^{-1} produced the maximum power density, current density, and COD removal efficiency of 137.6 mW m^{-2}, 0.28 A m^{-2}, and 72.0 ± 1.7%, respectively (Wang et al. 2015).

In another investigation, a double-chambered MFC operated with the white rot hydrolysed wheat straw generated 20.13 ± 0.052 mW m^{-2} of power density and provided the favourable growth condition for exo-electrogenic biofilm formation on the anode of MFC (Pal et al. 2023). The hydrolysate is usually rich in carbohydrates, soluble sugars, amino acids, nutrients, proteins, and other compounds favourable for microbial growth and helps to achieve high COD degradation and electricity production. Apart from the lignin-rich waste, livestock waste has also been utilised as an effective source for the electricity generation. For example, Zhang and their co-researcher operated the duel chamber MFC using dairy manure as the substrate, effectively recovering the highest of 14 W m^{-3} power density in long-term (140 days) operation (Zhang et al. 2015). The investigation also demonstrates that the hydrophobic acid and hydrophilic segment of the manure were the part of the dissolved organic matter and have been removed (around 80%) by the exoelectrogens persist in the anodic chamber of this dual chamber MFC. Performance of MFC reported in few other investigations using different types of agro-waste is presented in Table 4.1 with their required pre-treatment methods and output achieved.

Production of H_2 and other biogas by utilising agro-waste through MEC is a recognised superior electrochemical technology for H_2, CH_4, and other valuables' production by utilising the organic waste as substrate (Fig. 4.4b). The H_2 was found to be generated at low thermodynamic cell voltage of 0.2–0.8 V through MEC compared to conventional threshold voltage (1.23 V) of electrolysis (Rozendal et al. 2006). Apart from thermodynamic point of view, the MEC also has advantage over electrolysis for H_2 production such as low cost of electrode, no oxygen production, and no acidic electrolyte requirement (Rousseau et al. 2020). Hence, applying the agro-waste for simultaneous generation of electricity and H_2 can propel the waste treatment and circular economy. For instance, the Kadier and co-researcher operated the MEC for treatment of the palm oil mill effluent, and 1.17 m^3-H_2 m^{-3} day-COD was produced at pH of 6.3 with the dilution (59%) as pre-treatment of palm oil mill effluent (Kadier et al. 2022). The investigation focusing on agro-waste treatment with MEC suggested that the high COD complex nature of the biomass needs pre-treatment as it could be toxic for the exo-electronics. For example, the pre-treated palm oil mill effluent by ozonation (mg COD: mg ozone = 102.78) and the H_2 production (77.1 mL g^{-1} of COD) efficiency enhances by the 20% compared to raw palm oil mill effluent (Tanikkul and Pisutpaisal 2014). Apart from the oil mill effluent, utilisation of other agro-waste-based MEC operations with suitable pre-treatment is presented in Table 4.2.

Coupling dark fermentation (DF) with MEC has been investigated to ameliorate the production of bio-H_2 from agro-waste (Fig. 4.5a). The combined DF-MEC has advantage over the traditional DF system, as it does not get affected by VFAs and alcohol accumulation, the thermodynamic limitations, and pH variation of process

Table 4.1 Recovery of electricity by utilising agro-waste through a bioelectrochemical system

Agricultural stream	BES configuration	Pre-treatment	COD removal efficiency	CE (%)	Power density (mW m^{-2})	References
Rice straw	Air cathode single chamber MFC	Hydrolysis	72	17.9	137.6	Wang et al. (2015)
Corn Stover	Air cathode single chamber MFC	Steam exploded	60	1.6	406.0	Wang et al. (2009)
Wheat straw	DC-MFC	Hydrolysis and dilution	NA	37.1	123.2	Zhang et al. (2009)
Wheat straw	DC-MFC	Hydrolysis and dilution	95	17.0	148	Thygesen et al. (2011b)
Cheese way	DC-MFC	Not required	60	3.9	1.3	Kelly and He (2014)
Palm oil mill effluent	Up flow single chamber MFC	Not required	90	NA	44.6	Cheng et al. (2010)
Cereal processing effluent	DC-MFC	Not required	95	40.0	81.0	Oh and Logan (2005)
Mustard plant effluent	DC-MFC	Not required	57	15.0	45.5	Guo et al. (2013)
Brewery wastewater	Air cathode single chamber MFC	Not required	93	28.0	96.0	Zhuang et al. (2010)

CE-Coulombic efficiency, *DC-MFC*- Double chamber microbial fuel cell, *NA*- Not available

(Ndayisenga et al. 2021). However, the complexity of lignocellulosic compounds of agro-waste also possesses the challenge to DF-MEC. Hence, the pre-treatment of substrate becomes necessary for better yield of H_2 production through DF-MEC, and pre-treatment methods have been reviewed extensively in the latest literature (Awogbemi and Von Kallon 2022). The integrated DF-MEC system is usually operated in a two-stage process for converting the pre-treated agro-waste into H_2. Initially, the pre-treated substrate is fed to the DF chamber and optimise the conversion of substrate into VFAs, H_2, alcohols, and CO_2. Later, the effluent with high concentration of VFAs and alcohols (0.6 g-VFAs per g-VS) transferred to MEC for suitable conversion into H_2 by applying an external potential (0.2–1.0 V), which overpass the thermodynamic limit of conversion of VFAs to H_2 by the electrogenic

Table 4.2 Generation of biogas (H_2 and CH_4) through the hybrid bioelectrical systems

Agricultural stream	BES configuration	Pre-treatment	COD removal efficiency	Applied voltage (V)	Hydrogen/biogas production	References
Cassava starch	DF with single chamber membrane free MEC	Not required	58%	0.6	245 mL H_2 gCOD^{-1}	Khongkliang et al. (2017)
Waste sugar beet juice	DF with DC-MEC	Not required	57%	0.6	3.2 mol H_2 mol^{-1} hexose	Dhar et al. (2015)
Cheese way	DF with DC-MEC	Dilution	NA	1	94.2 L H_2 kgVS^{-1}	Moreno et al. (2015)
Cellulose	DF with DC-MEC	Not required	NA	NA	0.24 m^3 H_2 m^{-3}day^{-1}	Wang et al. (2011)
Wheat straw	DC-MEC	Hydrolysis	95%	0.7	0.61 m^3 H_2 m^{-3} MEC day^{-1}	Thygesen et al. (2011a)
Lignocellulos	DC-MEC	Alkali treatment	NA	0.8	28.67 L H_2 kg^{-1}	Zhang et al. (2019)
Rice straw	DC-MEC	Alkali and heat treatment	NA	0.8	2.46 mmol H_2 L^{-1} day^{-1}	Wang et al. (2017)
Straw	Combined AD-MEC reactor	Not required	NA	1	116.18 mL·CH_4 (g VS)$^{-1}$	Yan et al. (2022)
Swine manure	Combined AD-MEC reactor	Not required	NA	0.7	2.96 m^3CH_4 m^{-3}	Yu et al. (2019)
Dairy manure	Combined AD-MEC reactor	Not required	NA	1	143 L CH_4 (kgVS)$^{-1}$	Ding et al. (2021)

DF: dark fermentation, *DC-MEC:* double chamber microbial electrolysis cell, *AD-MEC:* anaerobic digestion microbial electrolysis cell, *NA:* not available

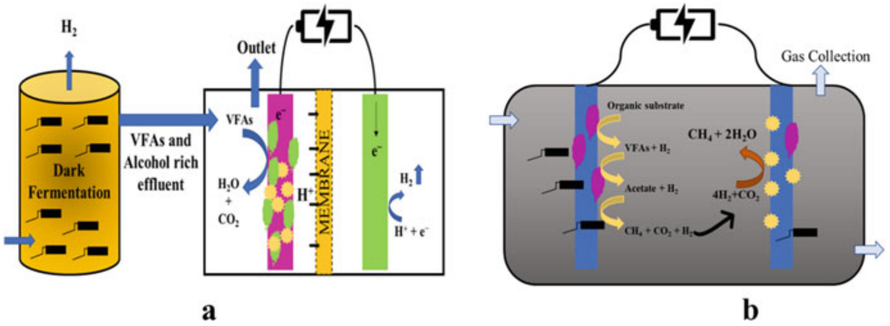

Fig. 4.5 The working diagram of hybrid Bioelectrochemical systems (**a**) DF-MEC (**b**) AD-MEC

bacteria. The investigations regarding the H_2 production by DF-MEC with the optimised parameters have been presented in Table 4.2.

Another significant gaseous product such as methane (CH_4) is also extensively recovered through MEC by the employment of different agro-wastes as substrate. The hybrid MEC, combining the anaerobic digestion and MEC, was examined for enhanced CH_4 production (Fig. 4.5b). Moreover, the widely spread anaerobic digester can be easily converted to the AD-MEC, and the methane production can be improved from 50% to 300% at an optimal 0.5–1.5 V power supply. The addition of the MEC enhances AD effectiveness by the prompt degradation of VFAs and other organic matter. Apart from it, AD-MEC transforms the microbial dynamics of the reactor by promoting the hydrogenotrophic methanogens compared to the acetoclastic methanogens (Wang et al. 2022). The hydrogenotrophic methanogens have a higher tolerance to pH, temperature, NH_4^+, and shorter generation time; these properties of the hydrogenotrophic methanogens enhance the methane production by tolerating the flux in these parameters. Few investigations focusing on the agro-waste have shown high methane production using AD-MEC (Table 4.2). The BES system either standalone or with combinations has shown good efficiency for the utilisation of the agro-waste; however, the investigation needs to overcome the limitations of electrode cost, extracellular electron transfer, and membrane cost involved in the BES. Thus, further investigation needs to focus on the synthesis of the different components of BES to overall reduce the cost of the fabrication and operations. The investigations regarding the utilisation of the agro-waste as the primary component for the membrane and cathode have been discussed below.

4.5.1 Other Applications of Agro-Waste-Derived Products in BES

The BES work on the principle of bioelectrochemistry needs highly efficient electrode and membrane for its operations. Usually, the carbon-based electrodes have been employed in BES fabrication due to its cost-effectiveness, high surface area, electricity conductivity, and good biocompatibility (Zhou et al. 2011). In addition to the electrode, the membrane and cathode catalyst also plays crucial role in the BES operation. For example, the investigation focusing on the distinctive commercial membrane found that the membranes such as Nafion 117 (514 $\mathrm{mWm^{-2}}$), CMI 7000 (514 $\mathrm{mWm^{-2}}$), and AMI 7001 (514 $\mathrm{mWm^{-2}}$) achieved different current densities due to their difference in the internal resistance, ionic conductivity, and proton transfer ability (Kim et al. 2007).

Similarly, the different cathode catalysts such as Pd (63.942 $\mathrm{mWm^{-2}}$, 25.82%) and Mn (63.942 $\mathrm{mWm^{-2}}$, 17.47%) nanomaterial have shown diverse power density and coulombic efficiency in the MFC based on their ORR potential (Das et al. 2020). Hence, the utilisation of the agro-waste based electrode, cathode catalysts, and membrane can reduce the overall fabrication cost of the BES and can incentivise the plant-based BES operations. For example, the membrane costs up to 50% of the overall cost, hence, the application of agro-waste-based membrane such as coconut shell, can reduce the cost of the MFC fabrication. Neethu and co-researcher applied the coconut shell as the membrane, and more power density (3.2 $\mathrm{W\ m^{-3}}$) was observed compared to the commercial Nafion membrane (1.8 $\mathrm{W\ m^{-3}}$). Furthermore, the oxygen mass transfer coefficient and proton transmission efficiency of coconut shell membrane was also comparable to the Nafion membrane (Neethu et al. 2018).

Apart from the raw coconut shell, the coconut shell char-based membrane was also investigated by the same research group and reported that the coconut shell-based membrane ($36 \times 10^{-6}\,\mathrm{cm^2\ s^{-1}}$) has more proton diffusion coefficient than Nafion ($4.64 \times 10^{-6}\,\mathrm{cm^2\ s^{-1}}$), consequently leading in more electricity production (Neethu et al. 2019). Researchers also investigated that the higher silica present in the agro-waste (rice husk and straws) accelerates the hydration property of the membrane, thus improving the membrane property. For instance, ceramic membrane modified with rice husk ash was explored in the MFC, and higher power density (2.14 $\mathrm{W\ m^{-3}}$) with lower ohmic (47.1 Ω) resistance was observed compared to the control membrane (2.14 $\mathrm{W\ m^{-3}}$, 91.3 Ω) (Raychaudhuri and Behera 2020). More detailed applications of agro-waste biomass in BES are listed in Table 4.3. Hence, the application of the silica or other similar oxide-rich agro-wastes can be a way forward to reduce the membrane cost in the BES application, resulting field-scale applicability of the system.

Moreover, the agro-waste-based cathode catalysts have also been explored to boost the oxygen reduction reaction (ORR) and power density of the BES. The activated char derived from agro-waste facilitates the higher ORR activity due to natural nitrogen compounds present in waste, such as pyridinic and pyridine (Yuan et al. 2014). The naturally present nitrogen compounds also create defects on carbon during char synthesis and upsurge the edge plane exposure, which further enhances the catalytic activity (Maldonado and Stevenson 2005). Apart from the nitrogen compounds, the agro char catalysts also found effective compared to the metal-based catalysts as it has long-term operational stability and is low cost and has higher chemical stability and good mass transfer capacity and electrical conductivity.

The investigations of olive mill waste-based char synthesis through pyrolysis were implemented as cathode catalysts in MFC, where 15 times more power density (271 $\mathrm{mW\ m^{-2}}$) was achieved as compared to the commercially available carbon black (17.3 $\mathrm{mW\ m^{-2}}$) (Sciarria et al. 2020). The higher power density of the Oliver

Table 4.3 The applications of agro-waste biomass in BES systems

Applications	Type of BES	Agro-waste	Inoculum	Power density (mW m^{-2})	References
As substrate	DC-MFC	Rapeseed cake	*Shewanella oneidensis* strain 14,063	33	Fernando et al. (2012)
		Corn steep liquor		39	
		Molasses		26	
	DC-MFC	Palm oil mill effluent	*Klebsiella variicola*	5.83 W m^{-3}	Islam et al. (2018)
As anode	DC-MFC	Coffee wastes	From domestic waste	3927	Hung et al. (2019)
	DC-MFC	Onion peels	Mix sludge	742	Li et al. (2018)
	DC-MFC	Compressed milling	Anaerobic mix sludge	532	Huggins et al. (2014)
As cathode	Air cathode MFC	Watermelon rind	From a stable operating reactor	0.262 W m^{-3}	Zhong et al. (2019)
	Air cathode MFC	Alfalfa leaf	From a stable operating reactor	1328.9	Deng et al. (2017)
	DC-MFC	Compressed milling residue	Anaerobic sludge	532	Huggins et al. (2014)
As proton exchange membrane	Air cathode MFC	Banana peel	Septic tank sludge	41.08	Chakraborty et al. (2020)
	DC-MFC	Coconut shell	Septic tank anaerobic sludge	3.7 W m^{-3}	Neethu et al. (2019)

DC-MFC: double chamber microbial fuel cell

mill waste was attributed to the oxygen and nitrogen compound present on the surface of the char. Apart from the cathode catalysts, the agro-waste has also been applied as the electrode material in the BES operation. As an example, the compressed milling residue anode (532 mW m^{-2}) produced the comparable power density (532 mW m^{-2}) to the commercial granular activated carbon and graphite granules (566 mW m^{-2}) (Huggins et al. 2014). The similar investigations focusing on the use of different agro-waste-based electrodes for application in MFC have been reviewed extensively in recent literature (Park et al. 2020; Mano 2020). In overall evolution, the application of the agro-waste can make the BES operation economically viable and can reduce the cost up to 90% compared to commercially available electrodes and membrane (Huggins et al. 2014).

4.6 Recommendation and Future Scope

Agriculture, being one of the largest sectors in the world, generates a considerable quantity of agro-waste. In the present era, the global perspective of agro-waste is changing fast in response to the need for environmental sustainability and conservation. Consequently, agro-waste is no longer regarded as garbage, rather a raw material for producing a variety of value-added products. However, reducing agro-waste generation by properly managing agro-products is still the best way to save the economic value and pollutant generation. The conversion of agro-waste to bioenergy is a sustainable solution to the agricultural sector's escalating refuse disposal problem and rising energy demand. The transformation of agro-waste to bioenergy can provide pure and renewable energy sources while reducing greenhouse gas emissions and promoting environmental protection. Furthermore, to fully realise the potential of agro-waste to bioenergy, certain recommendations must be followed, and future scopes should be explored.

Developing novel techniques and technologies is essential for bioenergy production from agricultural waste. This includes research and development in biogas production, biofuel production, and heat transfer. This will facilitate the efficient and cost-effective conversion of agricultural refuse into bio-energy. In this regard, BES for agro-waste remediation can be regarded as more sustainable than conventional conversion methods for producing valuable goods. Nonetheless, the BES is still in the embryogenic stage, and much research into the systems is necessary for their upscaling. Furthermore, very few articles are addressing agro-waste-based BES; thus, there is much scope for research in this area. Hence, future investigation for agro-waste remediation employing a BES system shall focus on factors such as water-to-agro-waste ratio, pre-treatment of agro-waste before being used as substrate in BES, and selection of microbial inoculum with respect to available agro-waste and reactor modification for better operation and outcomes. Upscaling of BES for practical application is still missing; bench-to-field-scale BES in this regard should also be investigated. The application of agro-waste-derived PEM and electrodes should also be investigated for the economic feasibility of the BES system.

4.7 Conclusions

The cutting-edge BES has substantial potential for producing bioelectricity and biofuels as well as recovering other valuables. However, the operating expenses associated with this advanced technique need to be reduced severely by developing inexpensive bio-based electrocatalyst and membranes, which would be a major step towards its commercialisation. Moreover, the productivity obtained through BES also needs to be ameliorated considerably, by employing easily available nutrient efficient agro-waste. Enhancing the yield of valuables acquired through fermentation would increase the revenue generated by these procedures, ensuring the economic and renewable sustainability of BES. Therefore, for the efficacious commercialisation and field-scale demonstration of BES, bio-based approach is essential to resolve the numerous roadblocks in the way towards the scaling-up of these inventive technologies.

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Energy-Efficient Bioelectrochemical System for Treatment of Agricultural Wastes and Wastewater: Mechanism, Scope, and Challenges

5

Dixita Phukan and Vipin Kumar

Abstract

Bioelectrochemical systems (BESs) have emerged as a potential new world technology in converting wastes to energy. A huge amount of persistent organic wastes are being produced from agro-based industries, and bioelectrochemical system has turned out to be an effective way of converting these agro-based wastes to energy and help in resource management. Bioelectrochemical system is not only efficient in minimising the organic contaminants but also useful in recovering nutrients. Agricultural organic waste can be used as feedstock for microbes while the treated wastewater can be reused again for irrigation water supply while generating power simultaneously. Moreover, this innovative technique generates negligible amount of toxic end products unlike other conventional techniques. Meanwhile this energy-efficient system can also be used in integration with the conventional techniques and contribute in generation of value-added products. Thus, this book chapter deals with the advances in the field of bioelectrochemical system for the removal of various organic contaminants from agricultural-based industries. The possible technologies to make it cost-effective will be reviewed along with the possible opportunities to scale it up with the use of minimal capital and resources.

Keywords

Bioelectrochemical system · Agricultural waste · Persistent organic pollutants · Nutrient recovery · Value-added products

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5.1 Introduction

With the increase in population, there is a growing demand for agricultural products as well. To meet this growing demand, various agro-based industries have been established, which require clearance of several acres of land for the cultivation of agricultural products. During the production of these agricultural products, a huge amount of organic wastes is produced, where some of them are recalcitrant as well and they skip the conventional wastewater treatment system. So as a result, various innovative technologies have emerged, and one such technology is the bioelectrochemical system (BES) which is equipped with microbes, and its integration with the traditional wastewater systems has proved out to be efficient and less time consuming along with generation of value-added products and green energy. Electrogenic microbes play a vital role in transferring electrons from/to electrodes (Logan 2009), and thus these microbes used in BESs carry out their metabolism by degradation of substrate which subsequently produces electrons and protons and these get carried to the cathode chamber containing electron acceptor agent through a series of carriers and thus enables the generation of electricity along with it (Rabaey et al. 2004). The effluents or wastewater from these agro-based industries once treated with bioelectrochemical system can be used for irrigation purposes, thus aiming towards sustainable agriculture.

5.2 Mechanism Behind Different Bioelectrochemical Systems Applicable in the Field of Agro-Based Industries' Effluents

Different types of bioelectrochemical systems have emerged up as an innovative and cost-effective technology for the treatment of various types of wastewater along with production of various value-added products, generation of biofuel, etc. An overview of the mechanism of different types of BESs is as follows:

5.2.1 Microbial Fuel Cell (MFC)

A microbial fuel cell is basically composed of an anode and a cathode chamber equipped with microbes which carry out oxidation of substrates supplied in the anode chamber, thus generating power along with it. The electrons produced in the anode by electrogenic microbes while feeding on the substrate are transferred through an external circuit to the cathode chamber. A proton exchange membrane in between both the electrodes helps in the transfer of protons from anode to the cathode chamber where it gets oxidised and form water molecules. Various mediators can also be used for the transfer of electrons from anode to the cathode chamber, and the microbes in the anode chamber transfer electrons to the electrode through C-type cytochromes and the use of soluble electron shuttles and by nanowires or pilli and electro-active biofilm formation. Electrodes made of different materials such as carbon cloth, carbon felt, graphite felt, and even electrodes

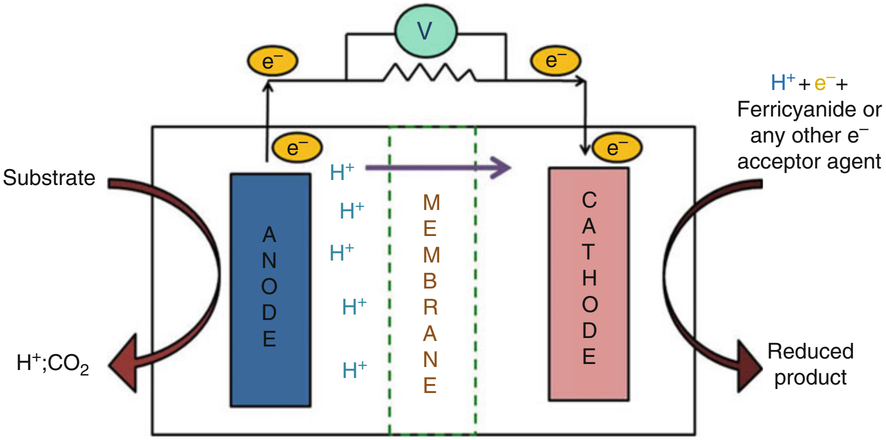

Fig. 5.1 Typical dual-chambered microbial fuel cell

fabricated with biochar have been used for the treatment of industrial effluents. The very first experiment of BESs using microbes for the production of electricity was introduced by M.C Potter where he made use of the bacterial species *Saccharomyces cerevisiae* to generate electricity in his study in (Potter 1911), (Fig. 5.1).

5.2.2 Microbial Electrolysis Cell

In microbial electrolysis cell, external power is being supplied onto the electrical circuit connecting the anode and cathode chamber for the production of hydrogen. In MFCs the cathode chamber is usually operated in the aerobic condition, whereas in case of MECs, the cathode chamber is operated in an anaerobic condition to facilitate the production of hydrogen fuel. Carbon dioxide produced in the anode chamber due to breakdown of the feedstock gets reduced in the cathode chamber and thus helps in generation of hydrogen. In a microbial electrolysis cell, the added advantage is that the external power supplied to the system for the generation of hydrogen is much less than the power supplied to a system for the electrolysis of water. If acetate is fed into the anode chamber as a substrate, then the reactions which take place in the anode and the cathode are as follows:

$$\text{Anode}: C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$$

$$\text{Cathode}: 8H^+ + 8e^- \rightarrow 4H_2$$

Studies were carried out using different configurations of MECs. Few of them are the following:

1. A two-chambered microbial electrolysis cell.
2. Concentric tubular microbial electrolysis cell.

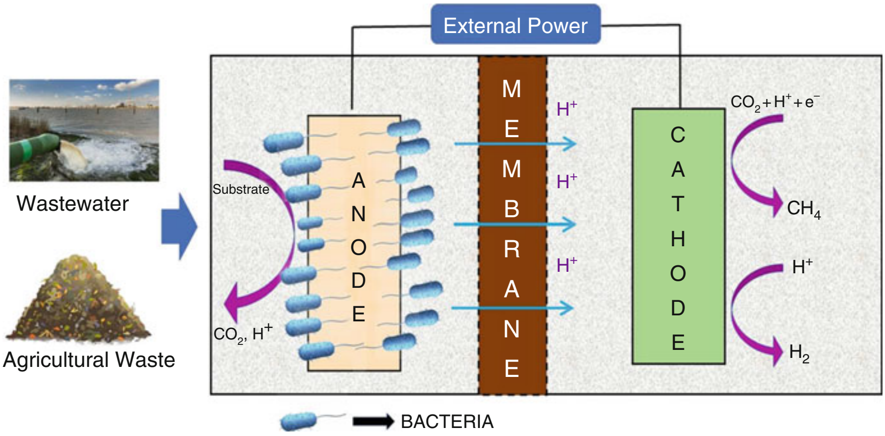

Fig. 5.2 A microbial electrolysis cell showing production of H_2 biofuel.

3. Bottle-type single-chambered microbial electrolysis cell.
4. Up-flow single-chambered microbial electrolysis cell.
5. Single-chambered glass tubular microbial electrolysis cell.
6. Microbial saline-wastewater electrolysis cell.
7. Microbial electrolysis desalination and chemical production cell and many more such configurations (Fig. 5.2).

5.2.3 Microbial Electrosynthesis Cell

In a microbial electrosynthesis cell, valorisation of carbon dioxide is carried out through microbial electrosynthesis for the production of various value-added products. Carbon dioxide valorisation can be carried out for the synthesis of various industrial products such as hexanol, butanol, butyric acid, acetic acid, hexanoic acid, and ethanol. If acetate is used up in the cathode chamber, then the reaction following the production of ethanol is the following (Fig. 5.3):

$$C_2H_3O_2{}^- + 5H^+ + 4e^- \rightarrow C_2H_6O + 2H_2O$$

In case of synthesis of butanol in the cathodic compartment, the following reaction takes place:

$$4CO_2 + 24H^+ + 24e^- \rightarrow C_4H_{10}O + 7H_2O$$

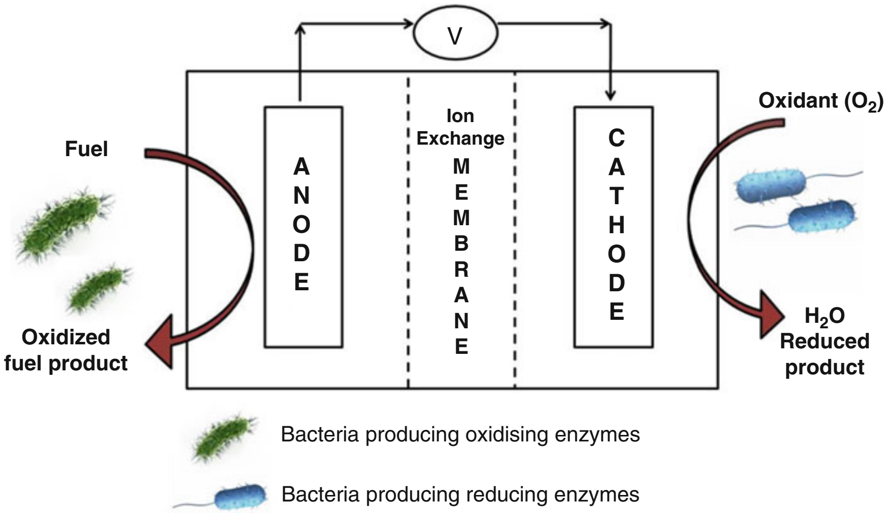

Fig. 5.3 A microbial electrosynthesis cell showing production of reduced and oxidised product

5.2.4 Microbial Solar Cells

In microbial solar cells, photoautotrophic small microbes or higher plants make use of the solar energy to carry out photosynthesis and thus oxidation of substrate which ultimately produces high-yield value-added products like methane, ethanol, hydrogen, etc. During the oxidation of the products, electrons are being produced by the electrogenic microbes which then gets transferred to the cathodic chamber where reduction of oxygen takes place, thus forming water molecules. These green phototrophic species help in the treatment of various industrial effluents, thus generating quite a good amount of electricity. In addition to that, these green pigmented species also aid in sequestration of carbon dioxide, thus helping to mitigate the greenhouse gases. Moreover in case of algal cells, the algal biomass which is being produced during the treatment can be further used as animal feed, fertilisers, and other value-added products. If implemented successfully, these systems can be used in agricultural fields, for easy production of agricultural products along with treatment of agricultural effluents which can be reused again for irrigation purpose (Fig. 5.4).

Reactions involved in a microbial solar cell are the following:

1. Photosynthesis is carried out by the plants using solar energy thus preparing their food:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (5.1)$$

2. The organic matter from the photosynthetic species gets transported to the anode chamber or substrate can be supplied externally as well.

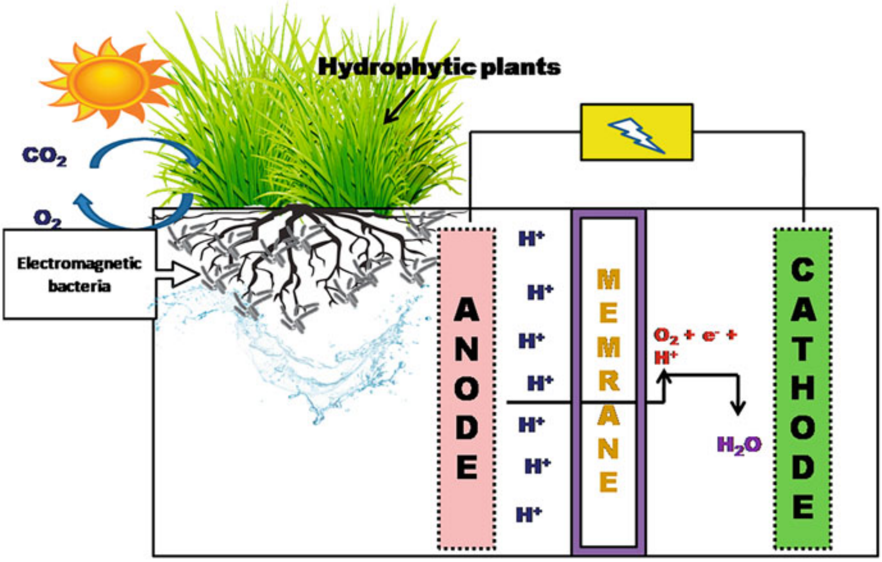

Fig. 5.4 A solar microbial fuel cell where photosynthesis takes place with simultaneous oxidation and reduction of substrate

3. In the anodic chamber, oxidation of the substrate/organic matter is carried out by the electrogenic bacteria:

$$C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^{\ -} + 30H^+ + 24e^- \tag{5.2}$$

4. In the cathode chamber, reduction takes place, thus leading to formation of water:

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \tag{5.3}$$

5.2.5 Plant Microbial Fuel Cells

Plant microbial fuel cells make use of different plants and their associated microbes in the anode chamber of the microbial fuel cell for the treatment of various polluted effluents. The roots of the plants are placed into the soil or water inside the anode chamber where the organic deposits from the roots or the rhizodeposits help to sustain the electrogenic microbes present in it. In this way, not only wastewater but also soil loaded with organic contaminants can be bioremediated by the microbes via utilisation of the organic contaminants as their feedstock. In this plant microbial fuel cells, electricity can be generated along with treatment of the wastes produced while harvesting, thus making agriculture sustainable (Fig. 5.5).

Reactions involved in both the anaerobic and aerobic chambers of plant microbial fuel cells are the following Regmi et al. (2018):

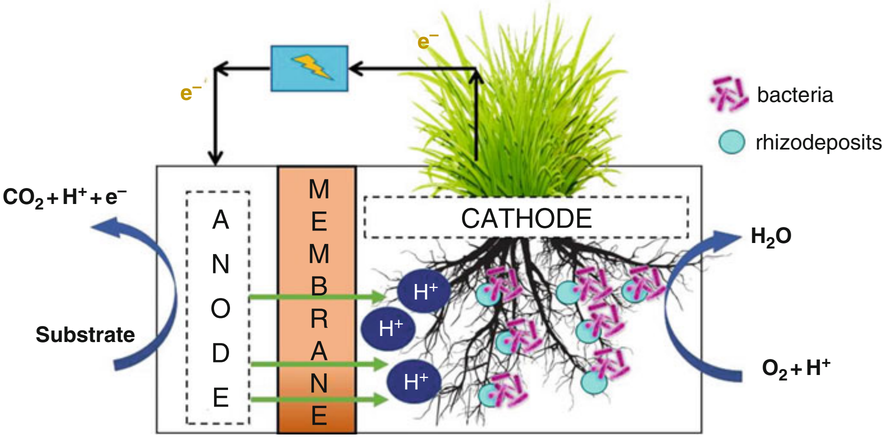

Fig. 5.5 Plant microbial fuel cell

$$\text{Anodic chamber} : C_{12}H_{22}O_{11} + 13H_2O(\text{Rhizodeposits}/\text{substrate}) \tag{5.4}$$

$$\downarrow$$

$$12CO_2 + 48H^+ + 48e^- \text{ (breakdown of substrate by microbes in anaerobic condition)} \tag{5.5}$$

$$\text{Cathodic chamber} : 48H^+ + 48e^- + 12O_2 \rightarrow 24H_2O \text{ or } 4H^+ + 4e^- + O_2 \rightarrow 2H_2O \tag{5.6}$$

5.3 Sources of Agro-Wastes from Different Industries and their Treatment with Different Types of BESs

5.3.1 Brewery Industry

According to Mathias et al. (Mathias et al. 2015), the different types of waste products produced in brewery industry are brewer's spent grain, hot trub, and residual brewer's yeast. A huge amount of brewer's spent grain (BSG) is being produced during the production of beer, and it is composed of complex carbohydrates, lipids, and proteins along with lignin and cellulosic and non-cellulosic polysaccharides (Lynch et al. 2016). It also contains a high amount of phenol which is not easily degradable. Moreover, the effluents from brewery industries contain high amount of BOD, COD, sugar, and alcohol levels and are usually low in pH. So efficient methods need to be used for its removal. Another waste produced from the brewery industry is the hot trub which refers to the sediments which is generated during the wort boiling process. It consists of tannins, malt particles, and complex carbohydrates along with polyphenols. If hot trub is not removed efficiently, it may form insoluble complexes which are highly undesirable.

Mathuriya and Sharma (Mathuriya and Sharma 2010) treated brewery wastewater using microbial fuel cell and demonstrated that it is feasible enough to treat brewery wastewater using mediator-less MFC and showed that with the addition of substrate such as glucose and acetate it can enhance the entire process. Negassa et al. (Negassa et al. 2021) isolated microbes from brewery wastewater, brewery waste sludge, and food processing wastewater and carried out the treatment of brewery wastewater, and it proved to be efficient enough for the removal of high levels of COD, BOD, and TDS, and the power density achieved during the experiment was 0.8 W/m^3 (for synthetic brewery wastewater) and 0.35 W/m^3 (for real brewery wastewater). Asensio et al. (Asensio et al. 2021) designed a microbial electrochemical fluidised bed reactor for the treatment of real brewery wastewater and found out that the percentage of COD removed was 87% and that of total nitrogen and total phosphorus were about 66% and 75%. Recently analysis of transformation of dissolved organic matter in bear brewery wastewater was carried out using bioelectrochemical system where it was found that the decomposition of dissolved organic compounds by microbes resulted into compounds having high hydrogen/carbon and low oxygen/carbon ratio. The microbes which were found to be dominating in the cathodic and anodic biofilm helping in the transformation of these organic compounds were *Zoogloea* and *Rhodococcus* and *Paludibaculum* and *Sphingomonas* (He et al. 2023).

5.3.2 Dairy Industry

The organic waste which is produced from dairy industry mainly consists of the raw milk and the milk products. According to Patra and Duary (Patra and Duary 2020), the sources of waste from dairy industry are the wastewater produced during the heating and cooling processes, spillage of milk during the production of milk products, also wastewater resulting from malfunctions in equipments, etc. The dairy effluents also contain a high amount of protein and fat residues and different additives. Dairy wastewater has the potential to deplete oxygen rapidly and thus form anoxic condition too.

Hasany et al. (2017) conducted an experiment on conditioned light and dark phase MFC to evaluate the efficiency, and he reported that though the light MFC (L-MFC) was quite steady than the dark phase MFC (D-MFC), both of the designs showed efficient results which was later converted to MEC for further enhancement of the process which showed better electrochemical performance and efficient removal of COD and other nutrients present in the dairy wastewater. In another study of dairy wastewater treatment conducted for 65 days at a stretch with similar two-chambered cells, it was found that 79–82% COD removal was obtained with a maximum power density of 26.5 W/m^3 (Callegari et al. 2018).

5.3.3 Edible Oil Industry

This industry as well generates a huge amount of wastewater, and it consists of high amount of COD, BOD, fats, oil, grease, and various other organic and inorganic substances which when disposed of can easily deplete the oxygen level in water and prove to be a threat to the aquatic organisms.

Yu et al. (2017) used microbial fuel cells and microbial electrochemical cells for the treatment of wastewater produced from refinery of edible oil produced from soybean along with production of bioelectricity and biomethane. The removal rate of COD by this experimental setup was found to be 95% along with sufficient yield of methane, and maximum power density achieved was 746 mW m^{-2}. Also palm oil mill effluent was treated with the help of microbial fuel cell and anaerobic membrane reactor where microbial fuel cell was used for preliminary treatment and the integration of MFC with anaerobic bioreactor showed better COD removal and worked as an efficient filtration system (Tan et al. 2017). Biosynthesis of waste cooking oil for production of biosurfactants was carried out with the use of a vertical and horizontally aligned microbial fuel cell, where it was found that the generation of current was directly proportional to the production of biosurfactants. The horizontally aligned microbial fuel cell was able to show better performance than the vertically aligned one, thus generating a power density of 4.84 Wm^{-3}(Pasternak et al. 2023).

5.3.4 Sugar Industry

The wastewater of sugar industry consists of a high load of organic pollutants. It is loaded with high amount of COD, total dissolved solids, chlorides, sulphates, oil and grease, and also heavy metals. It has been estimated that crushing down one ton of cane produces 1000 dm^3 of wastewater. Various researchers have found out that the total dissolved solids in sugar wastewater range approximately from 380 to 1700 mg dm^{-3}, whereas total suspended solids range from approximately 200 to 800 mg dm^{-3} and COD ranging between 1000 and 4000 mg dm^{-3}.

Siddique et al. (Siddique et al. 2018) carried out a study on potential of a lab-scale double-chambered microbial fuel cell in the generation of electricity using the sugar mill wastewater as a substrate with different concentrations. It was found out that with an increase in concentration of the substrate, there was an increase in generation of electricity as the organic content of the wastewater contained some amount of starch and glucose. Chaurasia et al. (Chaurasia et al. 2022) used electroplated co-metal electrodes fused in microbial electrolysis cell to carry out the treatment of wastewater from sugar industry along with effective production of bio-hydrogen and proved that MECs have the capability to generate value-added products from wastes, that is, bio-hydrogen from the sugar wastewater substrate.

5.3.5 Coffee Processing Industry

Wastewater from coffee processing industry consists of a high load of BOD up to around 20 mg L^{-1} and chemical oxygen demand (COD) up to 50 mg L^{-1} with acidic pH of approximately 4 (von Enden et al. 2002). Pulping of coffee beans increases the organic load of wastewater as pulping wastewater is composed of fermenting sugars and mucilage (particularly pectins which is composed of polysaccharides). It is also seen that the colour compounds from coffee cherries add colour to the wastewater, thus eventually turning water into blackish colour once it is dumped into the rivers from the coffee factories.

The wastewater from coffee processing industry was used as a feedstock in the anode chamber for the native microbes present in the wastewater, and it was found that through anaerobic oxidation process, COD was removed up to 65% and the power generation values reached up to 400 mV (Agudelo-Escobar et al. 2022). As per reports, per 100 mg of coffee contains 40 mg of caffeine, and caffeine is another substance of concern in the wastewaters of coffee processing industry. An up-flow wetland-microbial fuel cell was constructed for treating wastewaters containing caffeine, and this experimental setup was possible to achieve 90% decaffeination. Also toxicity assessments of caffeine were carried out along with decaffeination, and it was found that caffeine was broken down into less toxic products (Teoh et al. 2022).

5.3.6 Textile Industry

Cotton, jute, and silk are other such industries which make use of agricultural raw products for the production of textiles. Wastewater of these textile industries not only pollutes the surface water, but it also contains a lot of carcinogenic substances in it. Textile wastewaters are loaded with high amount of COD (1610–3200 mg L^{-1}), BOD (500–1000 mg L^{-1}), total dissolved solids (800–1600 mg L^{-1}), chloride (900–2500 mg L^{-1}), nitrate (100–650 mg L^{-1}), total hardness (100–150 mg L^{-1}), sulphate (200–2300 mg L^{-1}), and bicarbonate (500–1500 g L^{-1}) and also trace amounts of manganese, lead, copper, chromium, and iron. In addition to these, various natural and synthetic dyes are being used in the textile industries, and these are very recalcitrant in nature.

A hybrid system was constructed integrating a bioelectrochemical system, an anaerobic biofilm reactor, and a denitrification reactor all together for the treatment of wastewater from textile industries basically focussing on the removal process of the mixed dyes in it. Highly appreciable results were achieved through this setup where COD and total nitrogen decreased down to a level of 75 ± 18 mg L^{-1} and 12.91 ± 0.31 mg L^{-1}, along with removal of colour approximately around 48 ± 4 times, and the total phosphorus present in the wastewater reduced down to a permissible limit of around 0.5 mg L^{-1} (Cui et al. 2020). Another study was carried out using constructed wetland-microbial fuel cell (CW-MFC) system for the treatment of wastewater containing dye along with generation of electricity, and it was found that using this setup, it was able to achieve almost 70 ± 2% COD and 82.2 ± 1.7% ADMI in comparison to the freestanding constructed wetland system, and the maximum power density achieved using this hybrid system was 198.8 mW m^{-2} (Rathour et al. 2019). Dyes such as Victoria Blue R were removed from wastewaters of textile industry using a dual microbial fuel cell. Experiments were carried out using both synthetic and raw wastewaters containing Victoria Blue R, and in case of synthetic wastewater, COD removal was achieved up to a level of 98.7%, whereas in real wastewater, COD removal was estimated to be more than 96.6% along with removal of colour and ammonia, and the removal percentages were found to be more than 88% and 100%, respectively, and the power generated was more than 194.8 mW m^{-2} (Wu et al. 2020).

5.3.7 Rice and Wheat Mill Industry

Rice mill industry requires a huge amount of water for processing of rice which ultimately produces a lot of wastewaters. The rice mill effluents are loaded with high load organic contaminants along with traces of pesticides. In case of rice mill effluents, COD and BOD constitute the major source of pollutants. It is also loaded with high amount of dissolved and suspended solids. Likewise grinding and processing of wheat and various cleaning and packing operations in flour mill industry leads to high load of COD and BOD content in the wastewater. Wheat dust is another pollutant present in the wastewaters of flour mills which increases its organic load.

Three different MFCs were set up in different configurations; one was made up of earthen pot which itself worked as an anode chamber, and it was put in a plastic bucket which worked as a cathode chamber and another two dual-chambered MFCs were constructed using a proton exchange membrane for the treatment of rice mill effluent. Almost 87% of COD was removed using the earthen pot MFC, while with the other two MFCs, COD removal was achieved up to a percentage of 79% and 77%. Also phenol and lignin content in the wastewater was achieved more efficiently by the earthen pot MFC than the other two MFCs, that is, 84% and 81% (Behera et al. 2010). Rice mill wastewater containing high amount of lignin content was broken down into its by-products vanillic acid, benzoic acid, and muconic acid by lignin tolerant microbes in a dual-chambered microbial fuel cell. It was also found out that high load of COD in the wastewater was able to enhance the ability of microbes to generate a maximum power density of 0.4 W m^{-3} (Raychaudhuri and Behera 2023), (Table 5.1).

5.4 Challenges or Limitations in Proper Functioning of These Bioelectrochemical Systems

1. The membranes used in between these chambers are usually prone to fouling, and so the membrane needs to be changed at different intervals of time.

Table 5.1 Table showing a comparative study of removal of pollutants from different agro-based industries using BES

Sl no	Bioelectrochemical systems	Agro-based industry	Pollutant removal rate	Maximum power density	Reference
1	Microbial fuel cell	Brewery industry	COD79–83%	0.8–0.35 W m^{-3}	Negassa et al. (2021)
2	Microbial electrochemical fluidised reactor	Brewery wastewater	COD—87% Total nitrogen—66% Total phosphorus—75%	180A m^{-3}	Asensio et al. (2021)
3	Single-chambered air cathode BES reactor	Brewery wastewater	COD (closed circuit)—>80% COD(open circuit)—68%	38.0 ± 0.4 mW m^{-2}	He et al. (2023)
4	Microbial fuel cell	Dairy wastewater	COD—92% along with N and P removal	9.2 W m^{-3}	Hasany et al. (2017)
5	Microbial fuel cell (pilot scale)	Dairy wastewater	Removal of 82% organic matter COD—82–100%	26 W m^{-3}	Callegari et al. (2018)
6	Microbial fuel cell (MFC) and microbial electrolysis cell (MES)	Edible oil refinery wastewater	COD—96.4% for MFC and 95.8% for MES	24.1 W m^{-3}	Yu et al. (2017)
7	Horizontal microbial fuel cell	Waste rapeseed cooking oil	Initial – 1840 mg L^{-1} Final – 565 mg L^{-1} (vertical MFC) 899 ± 160 mg L^{-1} (horizontal MFC)	4.84 W m^{-3}	Pasternak et al. (2023)
8	Double-chambered microbial fuel cell	Sugar mill wastewater	Analysed as substrate for power generation	45–78 mW m^{-2}	Siddique et al. (2018)
9	Microbial electrolysis cell with Ni, Ni-co, and Ni-co-P electrodeposited cathodes	Sugar industry wastewater	COD – 50% removal rate	4.42 A m^{-2}	Chaurasia et al. (2022)

(continued)

Table 5.1 (continued)

Sl no	Bioelectrochemical systems	Agro-based industry	Pollutant removal rate	Maximum power density	Reference
10	Microbial fuel cell	Coffee processing industry	Removal of 70% of organic matter Cod—70–1005 removed	21.6 W m^{-3}	Escober et al. (2022)
11	Up-flow constructed wetland MFC	Caffeine containing wastewater	98% of decaffeination COD—> 96% removed	185.75 ± 25.20 W m^{-3}	Teoh et al. (2022)
12	Dual-chambered microbial fuel cell	Textile wastewater containing Victoria blue R (VBR)	VBR removal—99.8% COD—96.6% Colourity—88% NH3–100%	194.8 mW m^{-2}	Wu et al. (2020)
13	Earthen pot microbial fuel cell	Rice mill wastewater	COD – >85% Lignin – >75% Phenol – >75%	12.5 mW m^{-2}	Behera et al. (2010)
14	Microbial fuel cell	Rice mill wastewater	COD – 95% for 120–168 h, 66% after 264 h	4.3 W m^{-3}	Raychaudhuri and Behera (2023)

2. Although at the very beginning, it was developed with a concept of generating green energy but practically its power generation is very limited unless it is scaled up, it can be basically used for treatment of wastewater of small industries rather than focussing on generation of electricity.
3. The electrodes used in the systems are very expensive, and so efforts need to be made for the preparation of cost-effective electrodes.
4. A catalyst is required for enhancing the power generation in these systems, but again it adds to the cost and so cost-effective catalysts are required as well to make the entire system work efficiently for a longer period of time.
5. The problem of bi-fouling of membranes can be avoided by the use of membrane-less systems, but again in case of membrane-less systems, there is possibility of transfer of anolyte to the cathode compartment and vice versa.

6. More than half of the total cost is preoccupied by the electrode materials and membranes which again in long-term use leads to bi-fouling, and so research needs to be carried out on the development of cost-effective electrodes and membranes sustaining for a longer period of time.
7. The anode chamber is always prone to accumulation of proton making the anolyte acidic in nature which leads to inhibition of the microbes and thus permanent damage to the systems. Therefore, it is important to maintain neutral pH in the anode chamber throughout the process.
8. There is another possibility of substrate loss through diffusion. According to Kim et al. (Kim et al. 2007), substrate loss through diffusion is 3.7 times higher in case of anion exchange membrane-BES (AEM-BES) and then the cation exchange membrane-BES (CEM-BES) bioelectrochemical systems.
9. The microbes cannot survive in low temperature, so an optimum high temperature needs to be maintained continuously throughout the treatment process for sustaining the biofilm.
10. Usually there is insufficient electrode surface area for the microbes to sufficiently form a biofilm on it which again proves to be a hurdle in proper functioning of these systems.

5.5 Ways to Make BES Effective and Commercialisable

1. The electrodes are very expensive, and so attention needs to be drawn towards preparation of electrodes from easily available materials and also make it durable as well as biocompatible. Attempts are being made to prepare electrodes from biochar prepared from wood chips, reed, etc. Biochar electrodes are carbon rich and conductive and also have a large surface area for the microbes to form biofilm on it which makes it compatible for sustainable bioelectrochemical systems (Huggins et al. 2014; Wang et al. 2018; You et al. 2021).
2. Apart from electrodes, membranes occupy a huge part of cost of the bioelectrochemical systems, and research is being carried out on the preparation and usage of ceramic or earthen membranes, chitosan, etc. which are not only low at cost but also provide high mechanical and tensile strength along with improved electrical conductivity. Garchia and Ieropolous (Salar-García and Ieropoulos 2020) optimised terracotta clay-based membranes to analyse the performance of MFCs and found them ideal enough to be replaced with expensive polymer-based ion exchange membranes producing a power output of 94.67 μW cm^{-2}. A low-cost and environmentally friendly poly(vinyl) alcohol/chitosan membrane was prepared for generation of hydrogen biofuel in a two-chambered microbial electrolysis cell (MEC), and its hydrogen production yield was comparable to the MECs which used Nafion as a membrane. It was also able to remove acetate at a rate of 7% higher than that of Nafion membrane (González-Pabón et al. 2021).
3. Reactor geometry and function of electrode play a vital role in the performance of any bioelectrochemical system. Also less production of current in BESs in comparison to the capital cost invested on it proves to be a limitation in

commercialisation of these systems (Perazzoli et al. 2018). Study was carried out on treatment of brewery wastewater using a pilot-scale 90-litre stackable baffled microbial cell for a period of more than 6 months, and it was able to remove almost 85% COD and 82% suspended solids in case of diluted wastewater samples while producing a net electrical energy of 0.021 kWh m^{-3}, and in case of raw wastewater, the removal rate of COD and suspended solids were almost 88% and 86%, thereby producing a net electrical energy of 0.034 kWh m^{-3} (Dong et al. 2015). (Heidrich et al. 2014) also successfully carried out domestic wastewater treatment using a 100 L microbial electrolysis cell (MEC) for a period of 12 months, and in this pilot-scale study, they were able to achieve the yield of hydrogen at a rate of 0.6 L day^{-1} although the removal of COD was less than the prescribed standard limits.

5.6 Future Recommendations

1. As the conventional bioelectrical systems have quite a few limitations to it, so it can be made efficient and commercialised using hybrid systems, that is, integration of conventional treatments with bioelectrochemical systems which would not only provide convincing results but would also be sustainable as well.
2. As in most of these systems the electron acceptors are nothing but chemical agents, so there is always an opportunity to switch to bioelectron acceptors such as algae or other photosynthetic species which can later be used for generation of value-added products.
3. Mathematical modelling should be incorporated to understand the relationship of different parameters with that of generation of electricity and energy and nutrient recovery from different industrial effluents.
4. Although usage of these systems seems to be very advantageous, focus needs to be drawn towards its upscaling process for treating large volumes of wastewater and thus making this new world technology outshine in comparison to the conventional technologies.
5. For a bioelectrochemical system, it requires quite some time to recover from the toxic shock and get back to normal stable conditions and so it adds to the limitations of BESs, and hence more research is required in testing the systems in real conditions as most of the experiments carried out till now is basically on a laboratory scale (Grattieri et al. 2017).

5.7 Conclusion

Agricultural wastes and wastewater from agricultural fields and agro-based industries can be easily treated with bioelectrochemical and its integrated systems. Being self-sustainable, these systems not only aid in curbing the pollution content but also generate energy. For waste stabilisation, these agro-based wastewaters containing various organic compounds like lignin, cellulose, polysaccharides, and insoluble complexes can be used as feedstock for the microbes in the bioelectrochemical systems, thus breaking them down into smaller compounds and making agriculture much more sustainable. Scaling up and optimisation of these systems can prove to be a boon in the field of agriculture and various agro-based industries.

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Microbial Conversion of Agricultural Residues into Organic Fertilizers

6

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Abstract

Presently in developing countries, solid waste management is one of the crucial challenges since the need to use eco-friendly techniques appropriately increases alarmingly. Technological development, intensification, and urbanization of smart agriculture procedures have drastically accelerated waste generation from post-agricultural processes in recent years. Of course, the awareness of current technological implementation and the look for sustainability has provided a huge research platform for reducing unnecessary waste. From this context, the approaches, recycling, and microbial biotransformation are being applied to produce different valuable organic substances, such as high-quality bio-fertilizers. However, microbial approaches receive well appreciations due to their eco-friendliness. Besides, they can produce organic fertilizers that could significantly mitigate the impact of toxic chemical fertilizers. Consequently, microbial transformations are identified to recover macro- (N, P, and K) and micronutrients (Mg, Ca, Fe, Na, Mn, Cu, B, Zn, S, and Mo) and other value-added products. However, the fertilizers' characteristics may differ depending on the waste types. From this perspective, the chapter provides a comprehensive insight into agricultural waste management to produce organic fertilizers.

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Additionally, the trends, challenges, and prospects related to microbial methods of transformations are explored to consider the future development of sustainability perspectives.

Keywords

Agricultural residues · Microbial transformation · Bioprocess · Biofertilizer · Microbes

6.1 Introduction

The widespread use of chemical fertilizers significantly contributes to environmental degradation and contaminates water supplies. Deteriorating environmental conditions are a serious hazard to the world, resulting in soil fertility loss. Soil degradation and decreased fertility result from synthetic fertilizer use that is out of balance, negatively influencing agricultural productivity. The adoption of ecological and sustainable agricultural methods is currently acknowledged to be the only method for halting the downward trajectory in the world's productivity and environmental protection (Nagavallemma et al. 2006; Periyasamy et al. 2023; Mohamed et al. 2022).

In order to increase crop growth and production and supply and necessary food supplies, chemical fertilizers and pesticides have been widely used. To improve a plant's features and nutrient uptake, fertilization is essential. After extended periods of agricultural activity, nitrogen fixation will enhance crop growth and stop land degradation. Phosphorus is essential for energy metabolism, storage, and expression of genetic material (Chew et al. 2019). In this regard, many organic waste streams have high levels of nutrients (Rajesh Banu et al. 2021). Due to the possibility of eutrophication and other environmental issues, there have been more restrictions on releasing this garbage into the environment in recent years (Selvakumar and Sivashanmugam 2018a; Selvakumar et al. 2021). Nevertheless, current management frequently only considers this aspect and neglects to use recycled nutrients as resources to supplement mineral fertilizers. It takes a lot of energy to fabricate mineral (synthetic) fertilizers, especially when nitrogen is fixed, and mining for minerals is not sustainable over the long term. Particularly, phosphorus is predicted to become scarce in the next few millennia. Developing nations are challenging to obtain potassium at reasonable prices because it is only mined in Europe and Canada. Consequently, improved technologies for recycling nutrients from organic waste streams back into agriculture are needed to accommodate mineral fertilizers. There are several challenges in the approach to this, and societal and research adjustments are required (Foereid 2019).

Organic fertilizers and biofertilizers are two names for fertilizers derived from biological waste. Biofertilizers are materials with microbes; when they are incorporated into the soil, they make the soil more fertile and encourage plant development. By enhancing the delivery of vital nutrients to plants, biofertilizers containing microbes aid in stimulating the growth of plants and trees. Biological elements like bacteria, blue-green algae, and microbial fungi make up most of it. For the advantage of the plant, microbial parasites specially expel minerals from natural materials, while cyanobacteria are recognized by their capacity to settle nitrogen.

6.2 Classification of Biological Waste-Based Fertilizers (Biofertilizers)

Pollution and soil poisoning are the two big issues in the modern world. The environment has suffered greatly as a result of the usage of chemical pesticides and mineral fertilizers. Biofertilizer, an environmentally benign fertilizer presently utilized in most nations, is a solution to this problem. Biofertilizers are living things that improve the soil's nutrient content. The three primary biofertilizer sources are cyanobacteria (blue-green algae), fungi, and bacteria. The most striking connection between these and plants is symbiosis, in which both parties gain from one another. Moreover, biofertilizers can be grouped depending on the substrate or origin, the treatment or conversion method, or both. Buildups from agribusiness, ranger service, angling, aquaculture, nourishment preparation, sewage, and metropolitan squandering are the most sources of biofertilizers. Treatment alternatives include composting, vermicomposting, solid fermentation, drying, pyrolysis, and burning. Anaerobic digestion for the manufacture of biogas is another possibility. If heat is available, drying can be an alternative to minimizing the moisture content of organic waste biomass, like waste heat from power plants or the sun. There are also specific alternatives available for liquid waste streams, such as sewage and anaerobic digestate after biogas generation, with the main objective of suitably cleaning the water to be released to the recipient. Typically, mechanically dewatering and settling are used to separate solids. Precipitation chemicals (often iron aluminum) are employed to obtain soluble phosphorus in the solid phase (Foereid 2019).

Other than that, a biofertilizer is an overhauled natural fertilizer containing beneficial microorganisms. The constituents of biofertilizers encompass nitrogen fixers, potassium solubilizers, phosphorus solubilizers, and phosphorus mobilizers that can be employed alone or in collaboration with fungi. The majority of the microorganisms utilized in biofertilizers have intimate ties to plant roots. Legume roots and rhizobacteria interact symbiotically, and rhizobacteria live on root surfaces or in rhizosphere soil. The phosphorus microbes, primarily bacteria and fungi, give the plants access to insoluble phosphorus (Yimer and Abena 2019).

6.3 Conversion Technologies of Agricultural Residues for Farming Applications

The fabricating forms of natural fertilizers are exceedingly flexible and spin around the co-processing of natural and mineral frameworks. Organo-mineral fertilizers (OMFs) quirk dwells in utilizing systemic strategies for squander valorization to create cost-effective and eco-friendly items in the arrangement with the bio-circular economy. Synthesis of organic fertilizers from farming activities bio-waste utilizes the conversion technologies like chemical, physical, biological, and thermal methodologies. The main treatment or conversion technologies for agricultural residues and other organic residues are composting, vermicomposting, anaerobic digestion, drying, pyrolysis, solid fermentation, and combustion. Those technologies can be utilized alone or in integration.

6.3.1 Composting

Composting is one of the coordinates squander administration techniques utilized for reusing natural squander into a valuable item, as shown in Fig. 6.1. Composting includes the quickened corruption of natural matter by microbes beneath controlled environmental conditions. The natural fabric experiences a characteristic thermophilic organization that permits sanitization of the squander by the end of pathogenic microbes. To create compost, the organic matter must be rapidly degraded by microbes under regulated conditions. During this process, the organic material goes through a thermophilic stage that enables pathogenic germs to be removed from the trash, sanitizing it. Agricultural bio-waste composting can be divided into two processes. These encompass the thermophilic stage when a breakdown occurs more actively and serves the active phase of composting. The mature stage is characterized by a drop in temperature to the mesophilic range and a slower rate of degradation of the remaining organic molecules. The properties of the waste (quantity of readily biodegradable materials) and the manipulation of the controlling

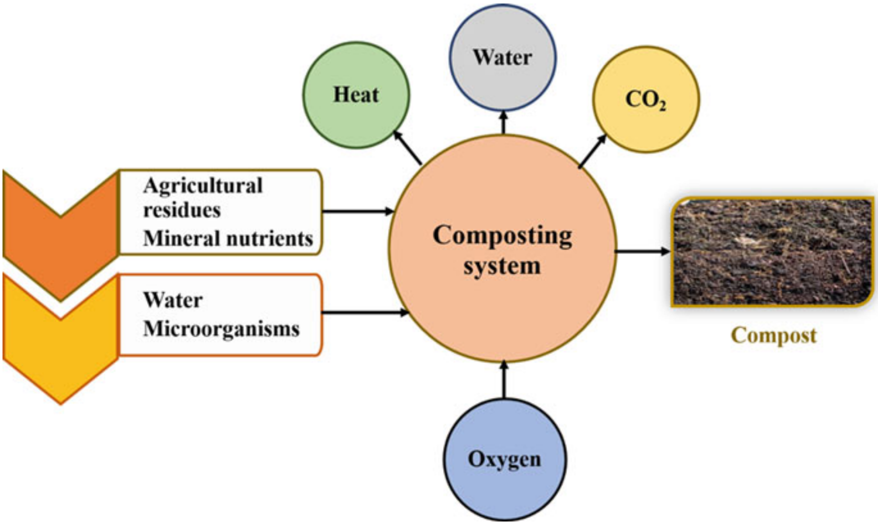

Fig. 6.1 Process flow chart of composting using agricultural residues (Corato et al. 2018)

parameters, such as aeration and watering, determine how long the active phase lasts. The maturity phase's length can also vary; however, it is typically identified by removing the phytotoxic chemicals. The industrial-scale treatment of solid organic waste by composting is well known. Still, one of the main drawbacks of the method is the loss of nitrogen caused by the volatilization of ammonia throughout the thermophilic stage (Lazcano et al. 2008).

It is simpler to manage and recycle lignocellulosic waste with high economic efficiency to compost agricultural wastes produced by the action of lignocellulolytic bacteria. Whenever applied to soil, recycled material improves the fertility and health of the soil. Composting is the biological stabilization and breakdown of an organic substrate under circumstances that permit the establishment of a thermophilic temperature as a consequence of heat generated by the organism. The temperature of the heaps rises as a mesophilic population develops during the earliest stages of composting by utilizing basic nutrients. In the subsequent phase, thermophilic microorganisms flourish. The finished product has the potential to enrich land due to its stability, absence of infections, and ability to plant seeds.

Organic wastes, including rice straw, sugarcane waste, and other agricultural wastes, have been disposed of using composting. Throughout composting, a natural succession of microorganisms occurs. Numerous fungi, including *Phanerochaete chrysosporium*, *Trichoderma harzianum*, *Pleurotus ostreatus*, *Polyporus ostriformis*, and others, are known to play a significant role in the composting of lignocellulosic biomass. It typically takes 180 days to compost agricultural wastes like paddy straw, which are high in lignocellulose, to deliver decent, mature compost. Due to the high lignin level, the cellulose in paddy straw is inaccessible to enzymatic and microbiological activity. Cellulose-degrading microbes speed up the biodegradation of crop leftovers, including straw, leaves, garbage, and other materials, and these cultures have been employed to compost plant waste (Singh and Nain 2014; Kavitha et al. 2022; Periyasamy et al. 2022).

Composting strategies vary in terms of deterioration and power of solidness and development. As a result of the biological and well-being concerns of human squanders, a broad investigation has been conducted to explore composting preparation and to look at approaches to portray the solidness, development, and sanitation of compost, sometime recently, its rural utilization, although a few examinations have tended to the optimization of composting, vermicomposting, or composting with consequent vermicomposting of different natural squanders. The characteristics of both composting and vermicomposting forms are displayed in Table 6.1.

6.3.2 Vermicomposting

One of the most effective ways to reduce and control environmental pollution is through vermicomposting. Vermicomposting is the method through which night crawlers and microorganisms work together to bi-oxidize and stabilize natural squander (Jayakumar et al. 2022). Vermicomposting is rising as the foremost fitting elective to ordinary oxygen-consuming composting. It includes the bio-oxidation

Table 6.1 Major characteristics of vermicomposting and composting in the agricultural bio-waste valorization

S. No	Differentiation criteria	Composting	Vermicomposting
1.	Definition	The process of biological oxidation and stabilization of waste organic material digestion by the actions of microbes	The process of biological digestion and stabilization of organic wastes by the combined actions of microbes and earthworms and to form the nutrient-rich product vermicompost
2.	Digestion mechanisms	Due to the action of microorganisms	Due to a couple of actions of earthworms and microorganisms
3.	Important stages	Mesophilic phase, thermophilic phase, cooling phase, and curing	Acclimatization, hydrolytic, and curing
4.	Heat levels	Compost piles are often heated because the aerobic breakdown of organic waste produces CO_2 and heat, resulting in piles that can reach temperatures of up to 150 °F. this is beneficial since heat can eliminate germs found in compost intake	Composting using worms is inherently colder, with temperatures ranging from 50 to 90 °F. the disadvantage of using less heat is that vermicomposting does not eliminate as many pathogens in the manure, waste food, etc.
5.	Microbial populations	As conventional compost piles can get heated, they are dominated by thermophilic (or "heat-loving") bacteria that flourish in certain conditions	Worm compost is dominated by mesophilic microbes that require more moderate temperatures
6.	Characteristics	Microorganisms: Major drivers for degradation of organic matter	Earthworms: Essential drivers such as grinders, aerators, and conditioners, finally improving the activity of microbes
7.	Processing speed	It is slow. A hot compost pile can take 6–9 months to complete the composting process	Faster process. Bin-type vermicomposting is a better choice and harvests the nutrient vermicompost within 8–12 weeks
8.	Final product	Compost, stable, humus-enriched, and complex mixture	Vermicompost and earthworm biomass are stable, disinfected, homogeneous, humus-enriched, and peat-like material and have higher nutrient content
9.	Cost	Cheap	Expensive
10.	Advantages	Waste sorting and pre-composting are not mandate, which is mostly preferable to industrial-level waste degradation	Economical, eco-friendly zero-waste technology, and fast
11.	Financial value	Cheap financial value	The much greater financial value

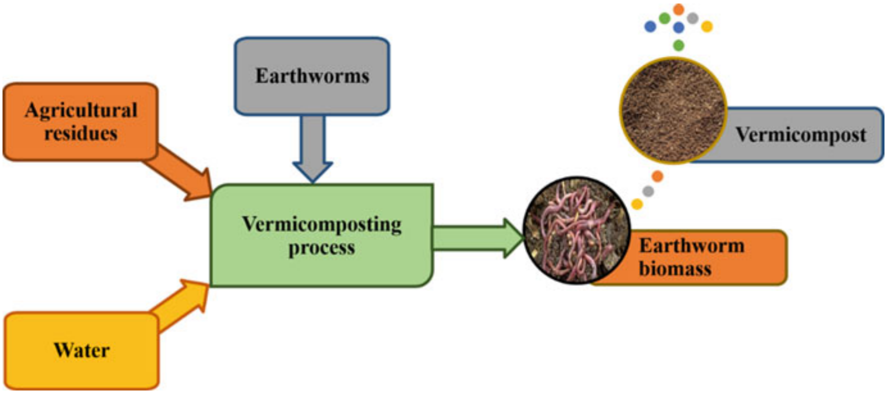

Fig. 6.2 Process flow diagram of vermicomposting practice using agricultural residues

and stabilization of natural fabric by the joint activity of worms and microorganisms (Karmegam et al. 2021). Process flow diagram of vermicomposting using agricultural residues is illustrated in Fig. 6.2.

Earthworms are the key players in the practice because they aerate, condition, and fracture the substrate, substantially affecting microbial activity, even though microbes biologically decompose the organic waste. By slowly diminishing the proportion of C: N and improving the surface region uncovered to microbes, earthworms operate as mechanical blenders and change the physical and chemical condition of the organic matter, making it much more conducive to microbial activity and further decomposition (Lazcano et al. 2008).

Earthworms active in the temperature range of 10–32 °C and mesophilic microorganisms work together through the vermicomposting process to transform agricultural bio-waste into the lucrative final product termed vermicompost. Contrarily, in composting, agricultural waste and its byproducts are degraded by microorganisms under regulated conditions, where the organic material goes through a distinctive thermophilic stage that enables the waste to be sanitized by getting rid of pathogenic germs. As a result of the combined action of enzymatic and microbial actions that occur throughout the process, vermicomposting produces an end product of greater quality than composting (Kaur 2020). Various stages of waste breakdown by earthworms occur during the vermicomposting process. The processes are specifically discussed below (Sharma and Garg 2018):

1. Agricultural organic waste material swallowing (ingestion).
2. Agricultural organic waste material is softened by earthworm saliva in their mouths.
3. Organic waste is softened and neutralized by calcium (excreted by the inner walls of the esophagus) and transmitted onto the gizzard for further action in the worm body's esophageal region.
4. In the muscular gizzard, waste is ground into smaller particles.

5. Organic waste digestion in the stomach by a proteolytic enzyme.
6. Degradation of cellulose pulp waste constituent materials through several enzymes released in the intestine, including proteases, lipases, amylases, cellulases, and chitinases, followed by absorption of the digested material in the intestine epithelium.
7. Undigested meal particles excreted from worm casting.

The practice of vermicomposting influences converts organic waste materials such as agricultural residues, cattle dung, and household waste into nutrient-rich organic fertilizers for plants and soil. Vermicompost may be a finely partitioned peat-like fabric with fabulous structure, good porosity, better air circulation, seepage, and moisture-holding capacity. Vermicompost, a natural fertilizer derived from the vermicomposting process, wealthy in nitrogen (N), phosphorus (P), and potassium (K) [NPK], presents macro- and micronutrients. Very useful soil organisms (nitrogen-settling and phosphate-solubilizing microbes and actinomycetes) could be a maintainable elective to chemical fertilizers, a fabulous growth promoter, and defender for trim plants.

The C/N ratio is significant for a multitude of composting processes, yet it is especially vital for the development of microorganisms since it offers the carbon and nitrogen sources needed for their growth. Restricting the amount of nitrogen is unfavorable as it slows down the carbon consumption rate, but instead, an excess of nitrogen might lead to an emission of NH_3 gas. As a result of carbon's conversion to carbon dioxide (CO_2) throughout the high-rate degradation stage, the C/N ratio measures the degree of digestion.

6.3.3 Anaerobic Digestion

Anaerobic digestion byproducts, known as "digestive waste," are nutrient-rich and might be reutilized as green fertilizers in farming, giving a feasible alternative for engineered fertilizers in cultivated environments. A green cultivated environment is a coordinated framework incorporating an anaerobic absorption biogas plant for squander treatment and natural fertilizer digestate for trim development. In such an agricultural ecology, AD biogas production is critical. On-farm anaerobic digestion (AD) converts waste organic matter into organic fertilizer, lowering expenses, diverting garbage from landfills, lowering methane emissions (mitigating climate change), and providing a low-carbon renewable energy source (Kavitha et al. 2021; Selvakumar and Sivashanmugam 2017b). Utilizing biogas in gas motors to form power and warmth can diminish buys of power and fossil fuels, whereas any additional power or heat can give extra cash. Biogas can be changed over to biomethane for infusion into the normal gas arrange or compressed into holders for utilization as fuel in other applications, such as street transport (SEAI 2020).

Waste, particularly waste biomass, is a vast feedstock bank that may be recovered using various methods and used to produce fertilizers. As a result, optimizing the synthesis of vital nutrients from biomass waste in a sustainable and ecologically safe

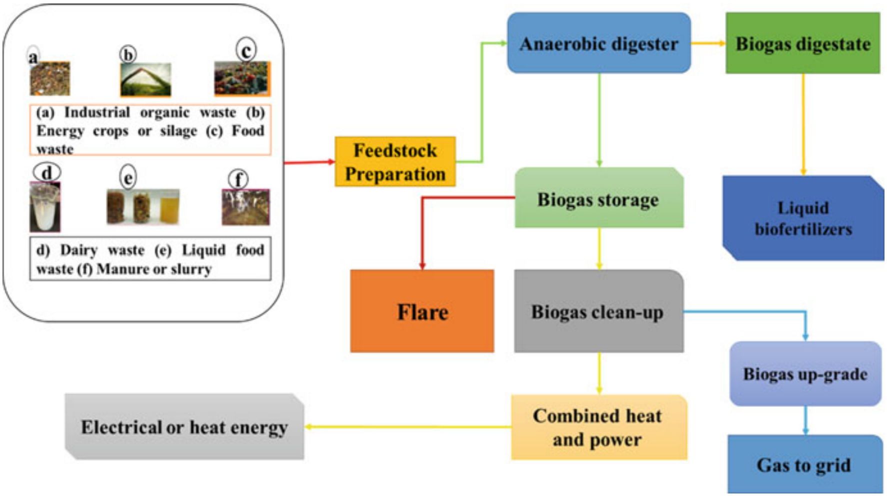

Fig. 6.3 Simplified process flow scheme for a farm-based anaerobic digestion facility

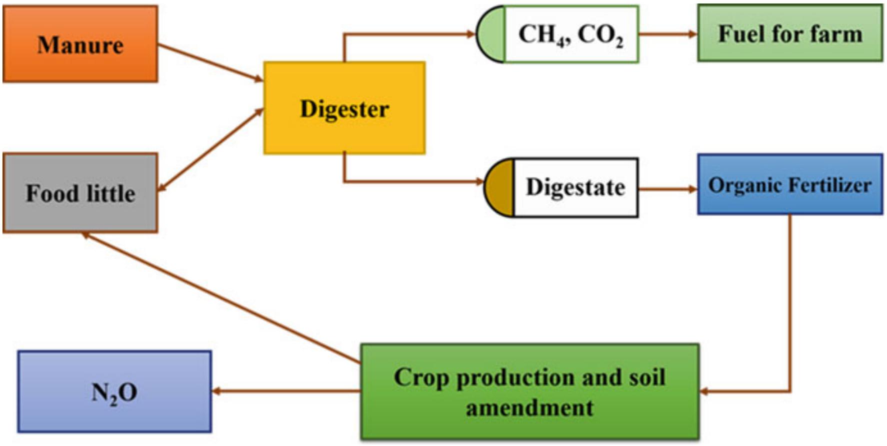

Fig. 6.4 The integration of AD biogas production with farm ecosystem

manner has become a major challenge in transitioning from a traditional fossil-based economy to a present-day bio-based and circular economy. Recent-day nitrogen fertilizer derived from livestock and poultry manure through biological synthesis can be used in place of synthetic mineral nitrogen fertilizer, coming about in a closed circle of rural nitrogen stream and more economical horticulture taking after the circular economy, as shown in Figs. 6.3 and 6.4 (Ogwang et al. 2021).

Controlling the anaerobic digester’s digestate output material is a vital success factor for anaerobic digestion (AD) systems. Digestate contains a high concentration of plant nutrients, primarily nitrogen, phosphorous, and potassium, as well as residual organic waste. It can be used as an organic fertilizer on agricultural land in the same way that animal manures and slurries are. This digestate requires land to spread, but it has considerable cost and nutritional benefits over raw slurries and chemical fertilizers. For instance, the full digestate produced by an AD tank can be distributed straight to agricultural land in its original state. Some processes separate the solid material into a solid cake (also known as "fiber" or "cake digestate") from the liquid portion of the digestate (sometimes referred to as "liquid digestate"). This is known as "dewatering," and it can be done in various ways, such as with filter presses or centrifuges. Fertilizers can be created by combining solid and liquid fractions. Solid cakes are a suitable option when there is a big distance to travel between the AD and the receiving land because they save the cost of carrying large volumes of liquid digestate, the majority of which is water. Solid cakes can be applied to the soil's surface and then plowed in. When sprayed on grassland's surface, liquid digestate has a lower viscosity than the whole digestate and may enter the soil more quickly. This indicates that it emits fewer emissions after application (SEAI 2020).

As an organic fertilizer, both fluid and solid digestate are high in nitrogen (N), phosphorus (P), and potassium, providing a sustainable option for synthetic fertilizer and recycling nutrients for organic crop production to offset the use of synthetic fertilizers. All natural fertilizers expand the potential natural nourishment yield for biological system cultivation. However, different feedstocks and AD treatments produce digestate with a different chemical makeup than undigested animal manures, which may have different effects on the soil microbial community and plant growth when used as fertilizers (Jin et al. 2022).

6.3.4 Solid-State Fermentation (SSF)

SSF is characterized as a procedure for developing microorganisms on strong, non-soluble materials within the nonattendance or close nonappearance of free water. SSF is displayed as a promising innovation for squander valorization through the bioconversion of natural squanders utilized as either substrate or dormant back. At the same time, microorganisms will play an incredible part in breaking biowaste into their components. The substrate or fermentation medium utilized for growing the microorganisms must meet their nutritional requirements. Filamentous fungi are the best type of microorganisms for SSF, as this culture technique mimics their natural habitat. In this regard, solid fermentation technology can convert agricultural biomass waste into organic fertilizers. The wastes disposed of in farming practices can be reutilized to prepare bio-organic fertilizers to supplement the synthetic fertilizers. In particular, the agricultural wastes used for the aforementioned purposes include crop residues, weeds, leaf litter, sawdust, forest residue, animal manure, and livestock waste. Most commonly, the wastes generated during the SSF operation are also utilized to synthesize organic fertilizers for crops' development and enhance soil amendment. Besides, to deliver high-quality crops, an elective to natural fertilizer is matured fertilizer, which is the title given to the effluents delivered within the maturation or absorption of natural squanders from solid-state fermenters (Yazid et al. 2017; Chontal et al. 2019).

Solid-state fermentation is divided into three stages: upstream, midstream, and downstream processes. The upstream process involves the preparation of substrates and growth media, as well as the isolation of microorganisms used in fermentation, followed by the midstream process, which involves inoculating and fermenting the substrate and finally the downstream process, which involves packaging the final products obtained. Even though the procedures involved in solid-state fermentation are widely used in industry, the methods used to get the desired end product to differ slightly (Yafetto 2022). The substrate is regarded as the carbon source in the fermentation process, which occurs in the absence of free water. Nonetheless, in the process of solid-state fermentation, the operation takes place in the absence or near absence of free water through the use of natural chemicals as well as a static substrate as solid support. Decomposition is another aerobic food waste disposal solution that turns waste materials into rich humus, enhancing conditions and plant soils. Solid-state fermentation, composting, and fermentation are alternative techniques for handling biological resources (Selvakumar et al. 2019a, b). These procedure modifications are in charge of converting food waste from fruits and vegetables into valuable resources such as organic fertilizers for agricultural use (Alfaili 2021).

6.4 Microbes Involved in Waste Conversion Processes

Waste conversion practices have received serious attention worldwide due to the global fertilizer supply and demand and the unsustainable nature of chemical fertilizers. Microorganisms are the key players in the waste conversion process that turns organic residues into valuable products such as compost, vermicompost, digestate, organic fertilizers, and other useful products (Selvakumar and Sivashanmugam 2018b, 2019). Various microorganisms, such as bacteria, mold, yeast, and fungi, are employed. These organisms are typically thought to be harmless and cannot affect consumers. Waste bioconversion produces goods like antibiotics, biogas, biofuel, biofertilizers, bioplastic, organic manure, organic acids, flavors, enzymes, nanoparticles, etc. (Selvakumar et al. 2018; Selvakumar and Sivashanmugam 2017a, 2020; Velusamy et al. 2021; Jayakumar et al. 2023). Numerous studies show that native isolates of bacteria, fungi, and actinomycetes can produce a variety of cellulolytic and ligninolytic enzymes that are useful in waste conversion processes.

6.5 Value-Added Products and Their Nutritional Importance

Esteem-included items are crude rural items (agricultural residues) that have been adjusted or improved to have better showcase esteem and/or a longer rack life value-added materials. A few illustrations incorporate natural products into compost, vermicompost, digestate, and biofertilizer. Plants require supplements for the same reasons that creatures require them. They require them to grow, develop, battle off infections and bugs, and replicate.

6.5.1 Compost

Compost is the ultimate item of composting that can be utilized as a revision for soils, as a development substrate for fancy and/or agricultural plants, and as a substrate for microbial inoculants. Compost benefits horticulture by giving assets and characteristic administrative instruments to replace exorbitant inputs that will hurt the environment, guaranteeing long-term agricultural sustainability. By-products generated throughout this approach include liquid and gaseous emissions, such as CO_2, CH_4, NH_3, and heat. Compost, formulated by the action of microorganisms on any waste, is widely employed as organic fertilizer for maintaining physical, chemical, and biological properties. The composting processes and the nutritional content of the compost are presented in Table 6.2.

Agricultural residues are one type of biodegradable solid waste that can be composted to create a soil conditioner. Compost has been shown to be of higher quality than inorganic fertilizers because it uses biological processes to recycle organic materials and nutrients into nutrient-rich soil. Microorganisms are used to carry out the process. In addition to giving plants the nutrients they need, compost also improves the soil's ability to retain water, carbon, and organic matter (Dutta and Suresh Kumar 2021). Additionally, compost can be a powerful tool for reducing soil greenhouse gas emissions in the agricultural ecosystem and sequestering CO_2 as soil carbon. The procedure can aid in soil bioremediation and act as a biological control for any pathogenic plant diseases. The primary components of compost are carbon and nitrogen, and factors like pH, electrical conductivity, moisture, the carbon-to-nitrogen ratio, temperature, aeration, and subpart size regulate the production process. It is a fairly straightforward process where highly biodegradable chemicals are transformed into stable organic matter for soil enhancement on-farm using small plants outfitted with instruments typically available to growers (Ganesh et al. 2021). There are four steps of compost processing (Corato et al. 2018):

1. Mixing basic materials rich in water, minerals, proteins, fats, carbohydrates, and dangerous microorganisms.
2. Building of compost piles to achieve adequate aeration of them.
3. Pasteurization is a process that uses bio-oxidation of organic molecules to produce heat, CO_2, and water to better sanitize food against pathogenic and hazardous microbes.
4. Final curing when finished compost has stabilized organic, carbon, nitrogen, phosphorous, micronutrients, heavy metals, water, and an array of beneficial bacteria that have completely or partially replaced those detrimental microorganisms.

Table 6.2 Summary of the composting process and compost nutritional value during agricultural valorization

Types of agricultural wastes	Composting agent/ method	Compost nutritional content	C/N ratio	Reference
Garden bio-wastes	Aerobic method	Macronutrients (10.00 g kg^{-1} N, 1.20 g kg^{-1} P, 4.50 g kg^{-1} K, 2.70 g kg^{-1} S, 13.4 g kg^{-1} Ca, 1.70 g kg^{-1} Mg, and 0.90 g kg^{-1} Na) and micronutrient (9.40 g kg^{-1} Cu, 8.80 g kg^{-1} Zn, 93.10 g kg^{-1} Mn, 5.80 g kg^{-1} Ni, and 214.30 g kg^{-1} Fe)	9:1 C/N	Jakubus and Michalak-Oparowska (2022)
Plant residues and mowed grass clippings	Aerobic method	Macronutrients (17.60 g kg^{-1} N, 4.80 g kg^{-1} P, 5.50 g kg^{-1} K, 2.90 g kg^{-1} S, 12.30 g kg^{-1} Ca, 1.60 g kg^{-1} Mg, and 0.90 g kg^{-1} Na) and micronutrient (8.10 g kg^{-1} Cu, 4.30 g kg^{-1} Zn, 99.50 g kg^{-1} Mn, 2.90 g kg^{-1} Ni, and 133.20 g kg^{-1} Fe)	9:1 C/N	Jakubus and Michalak-Oparowska (2022)
Mixed food and kitchen and garden bio-wastes	Aerobic method	Macronutrients (7.00 g kg^{-1} N, 7.90 g kg^{-1} P, 3.70 g kg^{-1} K, 1.40 g kg^{-1} S, 12.20 g kg^{-1} Ca, 1.4 g kg^{-1} Mg, and 1.40 g kg^{-1} Na) and micronutrient (9.60 g kg^{-1} Cu, 6.10 g kg^{-1} Zn, 113.80 g kg^{-1} Mn, 3.00 g kg^{-1} Ni, and 198.60 g kg^{-1} Fe)	12:1 C/N	Jakubus and Michalak-Oparowska (2022)
Rice bran (RB) and food waste (FW) (1 RB: 1 FW)	Accelerated degradation	27.18% TOC, 0.90% TN, 30.06% C/N ratio, and 45.12% VS, and 7.54 pH	30.06 C/N	Pourzamani and Ghavi (2016)
1 RB: 2 FW	Accelerated degradation	28.00% TOC, 0.99% TN, 28.69% C/N ratio, 47.52% VS, and 7.73 pH	28.69 C/N	Pourzamani and Ghavi (2016)
1 RB: 3 FW	Accelerated degradation	30.87% TOC, 1.06% TN, 28.06% C/N ratio, 50.42% VS, and 7.72 pH	28.06 C/N	Pourzamani and Ghavi (2016)
1 RB: 5 FW	Accelerated degradation	35.40% TOC, 1.25% TN, 27.33% C/N ratio, 58.40% VS, and 7.50 pH	27.33 C/N	Pourzamani and Ghavi (2016)

6.5.2 Vermicompost

Vermicompost is created when earthworms ingest organic matter and aerobically decompose it at room temperature with the help of micro- and macroorganisms. Additionally, vermicompost has a significant advantage over ordinary compost in that it is odorless, has a pH that has been corrected, has a low electrical conductivity, and has high concentrations of nutrients, including phosphorus, potassium, and nitrogen. Vermicompost is consistent and has a steady composition. In comparison to raw materials and other fertilizers, the contamination level is lower. Vermicompost is an efficient organic plant fertilizer due to the production of organic acids throughout the process and the presence of micronutrients, including iron, copper, and zinc. The effects of plant hormones that drive their growth are shared by organic acids, digestive tract secretions, and exudates from the surface of the worms, different enzymes, and humic acids. The resistance of the plant to diseases is caused by phenolic compounds produced in vermicompost. According to some research, vermicompost contains more humic compounds than compost. Because of the granulated feces of the worm, vermicomposting has a lower density than regular compost, which enhances the porosity of soil and the permeability of water in the soil. Water is available to plants for a longer period due to the vermicompost excellent humidity retention capacity. Unlike traditional composting, vermicompost is introduced during the thermophilic phase. Instead, earthworms use their digestive tracts to smash and slice organic materials, creating an aerated mass relatively devoid of pathogens, particularly coliforms. This sort of fertilizer is suitable for indoor applications. Earthworms alter the physical, biological, and chemical aspects of waste materials during the vermicomposting process. After 30 days of *E. foetida* earthworm activity, the final vermicompost was refreshingly earthy in odor, granular, nutrient-rich, much darker in color, and more consistent than the starting materials. The disintegration of organic matter in vermicompost is affected by several factors, including the nature of the feed substrate, aeration, moisture, temperature, and the earthworm species used in the process. As a result, they have an impact on final fertilizer parameters such as pH, electrical conductivity, TOC, TN, total phosphorus availability, total potassium, and metal content (Pourzamani and Ghavi 2016). Additionally, the major characteristics between vermicompost and compost are shown in Table 6.3.

Earthworm vermicompost is demonstrating its potential as a highly nutritive “organic fertilizer,” a more potent “growth activator” than traditional composts, and a “protective” farm input (enhancing the physical, chemical, and biological characteristics of the soil, rebuilding, and enhancing its natural fertility) against the “deleterious” synthetic fertilizers that have over time damaged the soil’s attributes and significantly reduced its fertility. The vermicompost manufactured from agricultural biowaste contains higher rates of nitrates, the more available form of nitrogen. The study also discovered that earthworm vermicompost contains more nitrogen and retains nutrients for a period. Vermicompost is a nourishing organic fertilizer enriched in nitrogen, potassium, and phosphorus, consisting of 2–3% nitrogen (N), 1.85–2.25% potassium (K), and 1.5–2.25% phosphorus (P), as presented in Table 6.4. There are also good amounts of calcium (Ca), magnesium (Mg), zinc (Zn), and manganese (Mn). In addition, enzymes such as lipase, amylase, chitinase, and cellulase that continue to degrade the organic matter in the soil are present in vermicompost. Besides, earthworm vermicompost contains micronutrients and essential soil microbes like mycorrhizal fungi and nitrogen-fixing bacteria, which have been scientifically proven to be miracle growth promoters and protectors during

Table 6.3 Major characteristics of compost and vermicompost

Classification criteria	Compost	Vermicompost
Description	It is formed by utilizing all types of agricultural and other wastes	It is fabricated from organic wastes
Contents of nutrients	It contains small amounts of nutrients such as nitrogen, potassium, phosphorus, and so on	It contains huge amounts of nutrients such as nitrogen, potassium, phosphorus, and so on
Requirement of space	During preparation, it requires a larger space	During formulation, it requires lesser space
Organic remains	Microbes decompose the organic residues	Earthworms degrade the organic residues
Kind of microbes	Thermophilic type of bacteria is utilized	Mesophilic bacteria are responsible for vermicomposting
Decomposition time	During the formulation of compost, more time is consumed	As it formulates compost in a faster period, it consumes less time
Mineral availability	Micronutrients and trace minerals are abundant	Plentiful in hormones, trace minerals, and micronutrients
Regulators of plant growth	It lacks plant growth regulators	Existence of plant growth regulators
Maintenance and labors	It needs more maintenance and more laborers	Need less maintenance and fewer laborers

farming activities. An adequate vermicompost application substantially increases soil enzyme activities like arylsulfatase, phosphodiesterase, urease, and phosphomonoesterase. Vermicompost-treated soil has a significantly near-neutral pH and higher electrical conductivity (EC) (Sinha et al. 2009). Moreover, the good criteria of vermicompost products are displayed in Fig. 6.5.

6.5.3 Digestate

The by-products of anaerobic assimilation, known as biogas digestate, can be utilized as a biofertilizer to make strides in soil richness and advance plant development. Digestate is a top-notch bio-organic fertilizer that is nutrient- and element-rich and high in nitrogen, phosphorous, and potassium (Chozhavendhan et al. 2023). It is also rich in organic matter, amino acids, vitamins, and some essential microbes. Additionally, it consists of trace elements like copper, zinc, manganese, magnesium, cadmium, and others. The aforementioned digestate components increase the humic material content of the soil and establish the basis for greater soil fertility. In recent years, the bulk of digestate has been employed directly in agriculture as biofertilizer, which is then converted into bioorganic fertilizer to improve soil fertility. Unfortunately, there are a lot of problems with using digestate directly. Between 50 and 80% of the total nitrogen in digestate coexists in the form of organic nitrogen and ammonium nitrogen, and the sluggish release of organically bound nitrogen reduces plant growth. Digestate has a gradual release phenomenon; thus they cannot entirely

Table 6.4 Summary of vermicomposting process and vermicompost nutritional value and other parameters during agricultural valorization

Types of agricultural wastes	Vermicomposting agent	Vermicompost nutritional content	Reference
Soybean meal, cow dung, elephant dung, coconut shell's hair, watermelon, and coffee ground	Earth worm (*Eudrilus eugeniae*)	1.108% N, 0.669% P, and 1.318% K	Khwanchai and Kanokkorn (2018)
Food and kitchen waste from households	Earthworm (*Eisenia fetida*)	Macronutrients (18.67 g kg^{-1} N, 5.30 g kg^{-1} P, 19.87 g kg^{-1} K, 4.23 g kg^{-1} S, 32.90 g kg^{-1} Ca, 8.77 g kg^{-1} Mg, and 1.73 g kg^{-1}) and micronutrient (16.00 g kg^{-1} Cu, 4.23 g kg^{-1} Zn, 86.37 g kg^{-1} Mn, 5.23 g kg^{-1} Ni, and 265.37 g kg^{-} Fe)	Jakubus and Michalak-Oparowska (2022)
Sugarcane bagasse and cattle dung (bagasse (B)): Cattle dung (CD) (B$_0$) (0:100)	Earthworm (*Eisenia fetida*)	1.08% total available phosphorus (TAP), 1.96% total potassium (TK), 2.00% TKN, 13.42% total sodium (TNa), 120.6 mg kg^{-1} Zn, 41.33 mg kg^{-1} Cu, 21.07 mg kg^{-1} Cr, 899 mg kg^{-1} Fe, and 181.4 mg kg^{-1} Mn	Bhat et al. (2015)
Sugarcane bagasse and cattle dung (bagasse (B)): Cattle dung (CD) (B$_{25}$) (25:75)	Earthworm (*Eisenia fetida*)	0.71% TAP, 2.47% TK, 1.77% TKN, 6.98% TNa, 130.2 mg kg^{-1} Zn, 29.57 mg kg^{-1} Cu, 26.83 mg kg^{-1} Cr, 998.90 mg kg^{-1} Fe, and 81.87 mg kg^{-1} Mn	Bhat et al. (2015)
Sugarcane bagasse and cattle dung (bagasse (B)): Cattle dung (CD) (B$_{50}$) (50:50)	Earthworm (*Eisenia fetida*)	0.68% TAP, 2.78% TK, 1.67% TKN, 7.75% TNa, 115.50 mg kg^{-1} Zn, 25.40 mg kg^{-1} Cu, 15.43 mg kg^{-1} Cr, 1030 mg kg^{-1} Fe, and 66.70 mg kg^{-1} Mn	Bhat et al. (2015)
Sugarcane bagasse and cattle dung (bagasse (B)): Cattle dung (CD) (B$_{75}$) (75:25)	Earthworm (*Eisenia fetida*)	0.40% TAP, 2.98% TK, 1.06% TKN, 3.88% TNa, 84.09 mg kg^{-1} Zn, 21.60 mg kg^{-1} Cu, 11.97 mg kg^{-1} Cr, 542.50 mg kg^{-1} Fe, and 35.10 mg kg^{-1} Mn	Bhat et al. (2015)

(continued)

Table 6.4 (continued)

Types of agricultural wastes	Vermicomposting agent	Vermicompost nutritional content	Reference
Sugarcane bagasse and cattle dung (bagasse (B)): Cattle dung (CD) (B_{100}) (100:0)	Earthworm (*Eisenia fetida*)	0.30% TAP, 3.26% TK, 0.86% TKN, 2.53% TNa, 60.63 mg kg^{-1} Zn, 15.47 mg kg^{-1} Cu, 22.77 mg kg^{-1} Cr, 459.10 mg kg^{-1} Fe, and 20.67 mg kg^{-1} Mn	Bhat et al. (2015)
Rice bran (RB) and food waste (FW) (1 RB: 1FW)	Earthworm (*Eisenia foetida*)	17.30% TOC, 0.95% TN, 17.85% C/N ratio, 28.47% VS and 7.49 pH	Pourzamani and Ghavi (2016)
1 RB: 2FW	Earthworm (*Eisenia foetida*)	22.99% TOC, 1.35% TN, 16.30% C/N ratio, 37.90% VS, and 7.58 pH	Pourzamani and Ghavi (2016)
1 RB: 3 FW	Earthworm (*Eisenia foetida*)	25.47% TOC, 1.62% TN, 18.16% C/N ratio, 42.12% VS, and 7.78 pH	Pourzamani and Ghavi (2016)
1 RB: 5 FW	Earthworm (*Eisenia foetida*)	30.13% TOC, 1.49% TN, 17.04% C/N ratio, 50.13% VS, and 7.82 pH	Pourzamani and Ghavi (2016)
Grass	Earth worm (*Eudrilus eugeniae*)	1.46% TN, 0.77% TP, and 0.77% TK	Klangkongsub and Sohsalam (2013)
Tomato	Earth worm (*Eudrilus eugeniae*)	1.37% TN, 0.68% TP, and 0.68% TK	Klangkongsub and Sohsalam (2013)
Tomato + grass	Earth worm (*Eudrilus eugeniae*)	1.57% TN, 0.89% TP, and 0.68% TK	Klangkongsub and Sohsalam (2013)
Haricot bean	Red worm (*Eisenia fetida*)	8.41 pH, 4.06 mS cm^{-1} EC, 57.39 meq/100 gm CEC, 21.26% organic carbon (OC), 775.39 mg kg^{-1} AP, 3.04% TN, 7.00 carbon to nitrogen ration (C/N), 6963.6 mg kg^{-1} AK, 11.59 meq/100 gm exchange K (EK), 26.80 meq/100 gm Ca, 13.20 meq/100 gm Mg, 29.56 mg kg^{-1} Fe, 354.35 mg kg^{-1} Mn, 4.24 mg kg^{-1} Cu, and 32.32 mg kg^{-1} Zn	Geremu et al. (2020)
Grass	Red worm (*Eisenia fetida*)	7.51 pH, 5.27 mS cm^{-1}, 57.39 meq/100 gm CEC, 34.66% organic carbon (OC), 1277.62 mg kg^{-1} AP, 4.26% TN, 8.14	Geremu et al. (2020)

(continued)

Table 6.4 (continued)

Types of agricultural wastes	Vermicomposting agent	Vermicompost nutritional content	Reference
		carbon to nitrogen ration (C/N), 4987.00 mg kg^{-1} AK, and 10.00 meq/100 gm exchange K (EK), 31.20 meq/100 gm Ca, 12.80 meq/100 gm Mg, 29.05 mg kg^{-1} Fe, 101.83 mg kg^{-1} Mn, 1.30 mg kg^{-1} Cu, and 35.81 mg kg^{-1} Zn	
Mixed straw	Red worm (*Eisenia fetida*)	8.09 pH, 3.69 mS cm^{-1}, 63.04 meq/100 gm CEC, 27.08% organic carbon (OC), 829.21 mg kg^{-1} AP, 3.73% TN, 7.27 carbon to nitrogen ration (C/N), 4571.50 mg kg^{-1} AK, and 20.72 meq/100 gm exchange K (EK), 32.00 meq/100 gm Ca, 10.00 meq/100 gm Mg, 38.23 mg kg^{-1} Fe, 120.87 mg kg^{-1} Mn, 2.67 mg kg^{-1} Cu, and 41.33 mg kg^{-1} Zn	Geremu et al. (2020)
Teff	Red worm (*Eisenia fetida*)	8.15 pH, 4.21 mS cm^{-1}, 68.70 meq/100 gm CEC, 27.00% organic carbon (OC), 1023.80 mg kg^{-1} AP, 3.77% TN, 7.16 carbon to nitrogen ration (C/N), 7327.70 mg kg^{-1} AK, and 20.92 meq/100 gm exchange K (EK), 35.20 meq/100 gm Ca, 12.00 meq/100 gm Mg, 54.24 mg kg^{-1} Fe, 117.66 mg kg^{-1} Mn, 0.90 mg kg^{-1} Cu, and 45.67 mg kg^{-1} Zn	Geremu et al. (2020)
Maize	Red worm (*Eisenia fetida*)	8.39 pH, 4.51 mS cm^{-1}, 66.09 meq/100 gm CEC, 28.21% organic carbon (OC), 987.38 mg kg^{-1} AP, 3.09% TN, 9.13 carbon to nitrogen ration (C/N), 4545.47 mg kg^{-1} AK, and 19.90 meq/100 gm exchange K (EK), 34.00 meq/100 gm Ca,	Geremu et al. (2020)

(continued)

Table 6.4 (continued)

Types of agricultural wastes	Vermicomposting agent	Vermicompost nutritional content	Reference
		12.00 meq/100 gm Mg, 46.01 mg kg^{-1} Fe, 105.14 mg kg^{-1} Mn, 4.20 mg kg^{-1} Cu, and 41.05 mg kg^{-1} Zn	
Sorghum	Red worm (*Eisenia fetida*)	8.43 pH, 3.29 mS cm^{-1}, 63.04 meq/100 gm CEC, 23.35% organic carbon (OC), 905.96 mg kg^{-1} AP, 3.16% TN, 7.39 carbon to nitrogen ration (C/N), 3740.40 mg kg^{-1} AK, and 18.97 meq/100 gm exchange K (EK), 34.00 meq/100 gm Ca, 12.00 meq/100 gm Mg, 46.02 mg kg^{-1} Fe, 112.03 mg kg^{-1} Mn, 6.67 mg kg^{-1} Cu, and 58.72 mg kg^{-1} Zn	Geremu et al. (2020)

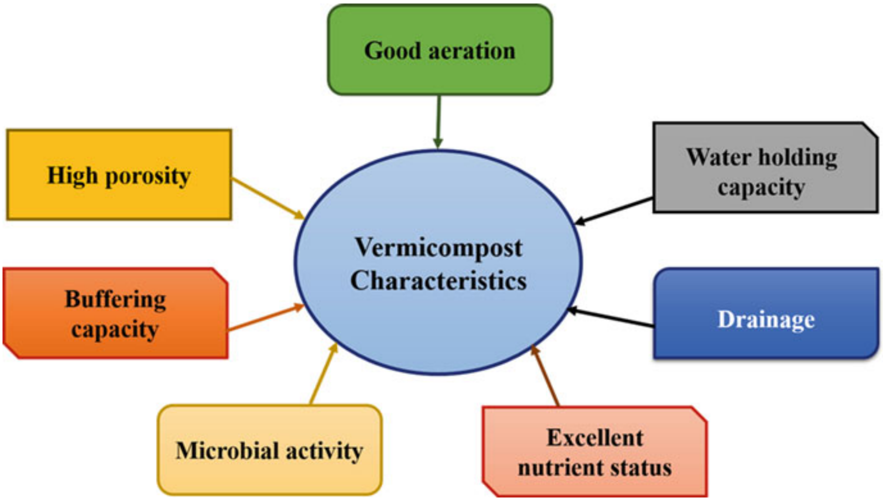

Fig. 6.5 Good criteria of vermicompost generated through the vermicomposting process

compensate for synthetic quick-acting fertilizers in agricultural activities. Additionally, ammonia volatilization from the direct application of digestate for agricultural activities to the soil results in nitrogen loss. The increment in nitrogen substance in normal soil and water, which comes about in eutrophication, is caused by ammonia

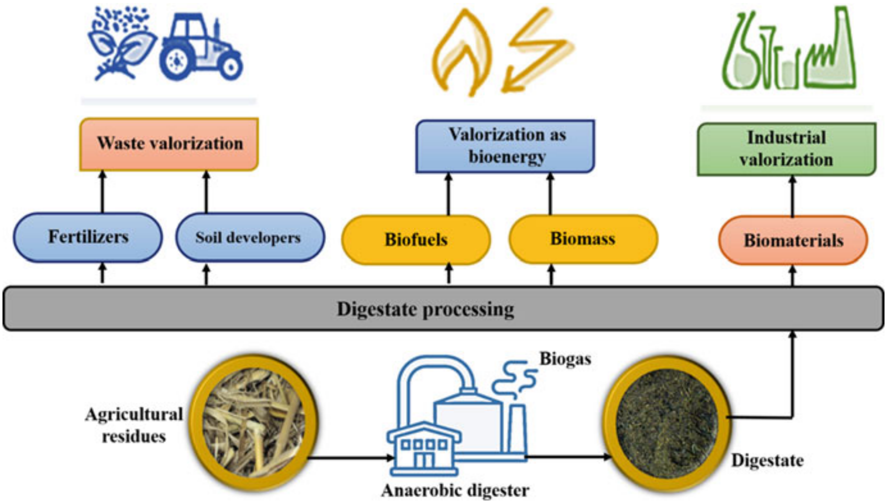

Fig. 6.6 Schematic diagram of digestate utilization (Guilayn et al. 2020)

nitrogen that has been volatilized and released into the atmosphere (Jin et al. 2022). The digestate valorization methodology has centered on arrival application, a compelling elective to commercial, natural, and squander recuperation (Tavera et al. 2023). Digestate utilization and production practices are presented in Fig. 6.6.

Digestate is a mixture of microbial biomass and undigested material that is produced in massive quantities in addition to biogas. To facilitate handling and transportation, digestate is often mechanically divided into liquid and solid parts. While the solid fraction primarily comprises phosphorous and residual fibers, the liquid fraction contains a substantial quantity of N and K. Due to these factors, digestate has attracted much attention as a fertilizer and soil enhancer over the past few decades due to these factors. Its use for farming has both financial and environmental advantages. For instance, it can supplement commercial fertilizers, which is crucial for recycling nutrient resources like phosphorus (Tavera et al. 2023). Digestate has a more diversified nutritional profile than unadulterated animal waste slurries, reducing the need for nutrient supplementation from traditional fertilizers when addressing crop nutrition requirements (Lee et al. 2021).

6.5.4 Biofertilizer

A biofertilizer is a substance that comprises bacteria capable of fixing nitrogen (N) and solubilizing phosphate to aid in the growth of plants. These microorganisms, which are referred to as "plant growth-promoting bacteria," infiltrate the soil and rhizosphere. It is a fertilizer containing living microorganisms that can be applied to seeds, plant surfaces, or soil to stimulate plant and agricultural growth. Biofertilizers are also characterized as an organism-based composition of micronutrients and carbon substrates that can feed and move soil quality, such as microbes, cyanobacteria, organisms, and green growth. Biofertilizers are materials that incorporate fertilizer and plant extricates that contain organisms that favor the development of the plant. This lesson of microorganisms is named plant growth-promoting microbes, a few of which advance plant development by settling climatic nitrogen and solubilizing phosphorus. Furthermore, biofertilizer can be clarified as a plan containing live or idle cells of microorganisms or their metabolites. Using natural fertilizers in agribusiness can reduce the poisonous quality of chemical fertilizers. Also, the business of natural squandering for fabricating biofertilizers can moderate the impact of natural contamination that can harm human well-being (Hapsoh et al. 2020).

As a result of increased soil acidity brought on by prolonged use of chemical fertilizers, soil friability is damaged, affecting crops in general and soil microorganisms in particular. With the use of biofertilizer, the soil fertility cost is maintained while production is guaranteed, and continued use of biofertilizer makes the soil extremely fertile for good yield (Kumar et al. 2021; Mohod et al. 2015). Vermicomposting and composting provide nutrient-rich materials that are great sources of biofertilizer for plant growth. Biofertilizers, made from natural buildups, seem supplant a few mineral fertilizers, diminishing vitality utilization and asset mining, and are utilized to keep the soil from losing more supplements (Foereid 2019; Dutta and Suresh Kumar 2021). Straw and rice bran are two examples of agricultural waste that are used as the base for biofertilizers. These materials are converted into organic fertilizer after being safely disposed of and fermented. Consequently, organic fertilizer is rich in nutrients, including nitrogen, phosphate, and potassium, and contains a range of organic acids and peptides (Kumar et al. 2022). Along with providing crops with complete nutrition, fertilizers also have a lasting impact on soil organic matter, encourage microbial breeding, enhance the physical and chemical characteristics of the soil, and increase biological activity (Namfon et al. 2019). Traditional chemical fertilizers become much more effective and less necessary when using biochar, dramatically improving crop yields. Biofertilizers do not contain the same levels of N, P, and K as conventional fertilizers. Nearly 0.45, 0.81, and 2.93 g kg^{-1} of N, P, and K are present in biofertilizers. Agricultural wastes like rice husk can be used as chemical fertilizers, herbicides, insecticides, and other things (Sharma et al. 2020).

6.6 Trends and Prospects

Today the greatest attention across the globe is devoted to the agriculture sector because their contribution is usually irreversible and very essential in the socioeconomic improvement of any country. As per the present agricultural scenario, the importance of agriculture has increased considerably and is expected to increase further with the rapid urbanization, commercial activities, and population growth of the world. Hence to face the fertilizer demand shortly, more focus and attention will be given to sustainable organic fertilizers like compost, vermicompost, digestate, and biofertilizer from agricultural residue waste materials. Regular application of chemical fertilizer pollutes the land, increases soil corrosion, and kills the naturally present microbes. To overcome this problem, the development of organic nutrient-rich compost, vermicompost, digestate, and biofertilizer production practices is essential. Composting, vermicomposting, anaerobic digestion, and SSF practices are the most promising, globally accepted, and environmentally friendly technologies for compost, vermicompost, digestate, and biofertilizer production. The researcher's background will typically determine their agenda for future study in some areas where research is required regarding the perceived value of research in various areas. Even so, it can be difficult to determine at a small scale how easily observable fundamental factors can be utilized as markers for more complicated processes and to support effective control of composting, vermicomposting, anaerobic digestion, and SSF operations.

Sensors need to measure gas phases to address this problem and eliminate the need for time-consuming and laborious operations. This may increase prospects for improving composting, vermicomposting, anaerobic digestion, and SSF facilities. DNA sequencing has become considerably more inexpensive in the current era of next-generation sequencing than earlier. This is a chance for researchers to use sequencing methods to provide a correct and comprehensive understanding of the microbial populations and enzyme activity in composting, vermicomposting, anaerobic digestion, and SSF operations. These enzyme activities include the creation of greenhouse gases, the formation of organic waste, and the manufacturing of odors.

6.7 Conclusions

In this chapter, a detailed discussion on the conversion technologies composting, vermicomposting, anaerobic digestion, and SSF process, microbes involved in waste conversion processes, value-added products, and their nutritional importance trends, challenges, and prospects were discussed. Furthermore, the pros, cons, and challenges were also discussed briefly. However, this chapter indicates that further technological development in various compost, vermicompost, digestate, and biofertilizer production-related areas is essential for process improvement that combines all available options on various aspects to decode this technology into an excellent choice for sustainable development in the future.

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7 Thermochemical Approach for Sustainable Transformation of Agricultural Waste into Value-Added End Products

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Abstract

Agriculture is the source of food, clothing, and survival for human beings. The stable development of agriculture directly affects national economic development and social stability. A large amount of agricultural waste can be generated in the agricultural production process, such as crop straw, livestock manure, agricultural film, pesticide packaging waste, etc. If these wastes are not handled properly, they may not only cause waste of resources but also lead to environmental pollution. Therefore, how to realize the above agricultural waste recycling and high-value utilization has become a current research spot. As a kind of clean and renewable energy, agricultural waste can be recycled and transformed into high value-added products, such as bio-hydrogen, biochar, biogas, biodegradable tableware, etc., which could be considered "turn waste into treasure." This can not only promote the sustainable development of agriculture and energy conservation and emission reduction but also realize the "double efficiency" of economy and ecology. Recently, although some progress has been made in the thermochemical conversion technology of agricultural waste worldwide, there are still some problems to be resolved and digested to achieve its efficient utilization. For example, it is necessary to systematically explain the thermochemical conversion process, evaluate the utilization rate and quality of thermochemical conversion, and investigate the impact of operating conditions and parameters in practical applications. Therefore, this chapter will focus on several typical thermochemical methods (including torrefaction, pyrolysis, gasification, and hydrothermal carbonization) and improve thermochemical processes (including microwave and

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integrated thermochemical processes) and then analyze the influencing factors in the practical application and their respective advantages and disadvantages. On this basis, the advantages and disadvantages of current chemical conversion technologies of agricultural waste and the future development trend are proposed.

Keywords

Agricultural waste · Thermochemistry · Sustainable · Operating conditions · Energy

7.1 Overview of Agricultural Waste

Agriculture is the source of food and clothing for human beings, the basis of survival. At least 1.3 billion tons of agricultural waste is annually produced worldwide. Therefore, how to dispose of agricultural wastes properly and make full use of them has become a common challenge worldwide. Traditional methods of agricultural waste disposal mainly include incineration and landfill, but these methods may result in water pollution, air pollution, and even a series of environmental health problems. To improve the utilization rate of agricultural waste and reduce its impact on the ecological environment, a large number of studies have been carried out globally in the past. For example, India, the second largest agricultural country, generates millions of tons of agricultural waste every year that has been converted into biogas for power generation, alleviating the energy crisis (Kapoor et al. 2020). The United States also produces millions of tons of agricultural waste every year, but they use hydrothermal carbonization technology to convert most of the wastes into many high-value water-soluble organic matter (including sugars and organic acids) (Hoekman et al. 2011). In addition, coffee husk waste is decomposed through pyrolysis to produce important industrial products such as methanol, acetic acid, and hydrogen in Brazil (Song et al. 2020). However, the composition of agricultural waste from different sources is different, and different thermochemical conversion technologies have their limitations. As a result, different technologies show different effects during the application process. To better understand and master the advantages, disadvantages, and performance of different technologies, it is necessary to introduce several typical thermochemical conversion technologies in agricultural waste in detail in this chapter. At the same time, the challenges of current thermochemical technology and the direction of further development are put forward to promote the utilization of agricultural waste resources.

7.2 Conversion Technologies

7.2.1 Torrefaction

Torrefaction is a biomass thermochemical conversion technology. Since Bourgois discovered that carbon-rich products (biochar) could be obtained after pine wood torrefaction in 1988, torrefaction technology has been widely used in biomass thermochemical conversion (Niu et al. 2019). According to the treatment medium (Table 7.1), it can be divided into dry torrefaction (DT) and wet torrefaction (WT). Among them, DT reduces the oxygen content of agricultural waste and increases the energy density of products. In contrast, wet torrefaction allows the treatment of agricultural waste with high water content and the enrichment of renewable compounds.

Generally, agricultural waste is first pre-dried at 100 °C to reach the drying temperature, and then the temperature is increased to 200 °C for post-drying and finally baked and cooled to produce solid products, gas, etc. (Fig. 7.1) (Kota et al. 2022). The entire torrefaction process is divided into three stages according to thermogravimetric analysis (TG). The first stage, namely, the torrefaction stage, shows the first peak on the TG curve due to the weight loss caused by the evaporation of water. In the second stage, namely, the devolatilization and depolymerization stage, the decomposition of hemicellulose, cellulose, and a small portion of lignin in agricultural waste occurs, and the second peak in the TG curve appears. The third stage is the continuous torrefaction stage when the rate of weightlessness has not changed significantly. Besides, the structure and physicochemical properties of the agricultural waste change accordingly during the torrefaction process. Functional groups (O-H, C-H, and C=O) decrease with the release of H_2O, CO_2, CH_4, and CO. And the fixed carbon content and moisture content will increase with the

Table 7.1 Difference between wet and dry torrefactions

Torrefaction types	Conditions	Products	Advantages
Dry torrefaction (DT)	200–300 °C 5–120 min 1 atmospheric pressure	Solids, volatiles (H_2, CH_4, CO), etc.	DT helps to reduce by-product yields and improve bio-oil quality during rapid pyrolysis Simple and easy-to-operate process High ash retention and high deaerating properties High biochar yield
Wet torrefaction (WT)	180–260 °C 5–120 min 1–200 atmospheric pressure	Solid phase, gaseous, and aqueous by-products	Reducing the hydrogen, nitrogen, and sulfur content of biomass to lower values Preserve active hydroxyl groups to ensure cellulose order Effective handling of wet or even extremely wet biomass materials High hydrogen storage

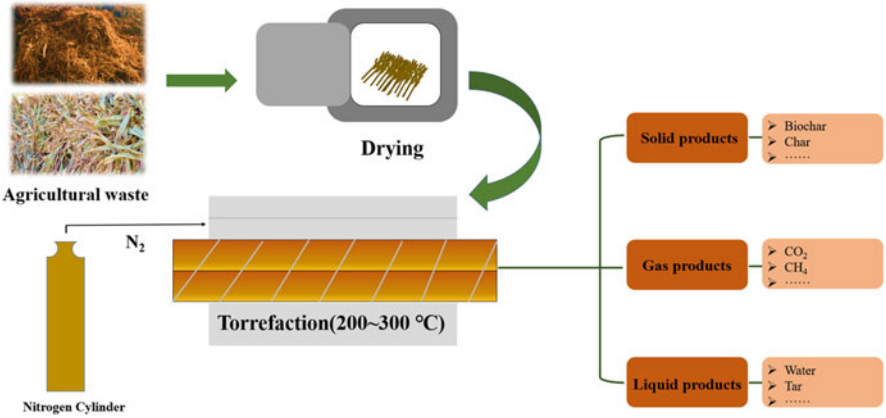

Fig. 7.1 Torrefaction process and products

increase of temperature during the torrefaction process. Currently, low-temperature torrefaction of agricultural waste mainly produces value-added products such as biochar and biomass coal. For example, agricultural wastes (such as rice husks, peanut shells, and wheat straws) have been prepared into low-cost biochar adsorbents by torrefaction and used to adsorb organic and inorganic pollutants in water (Zhang et al. 2018). A large amount of cellulose-rich agricultural wastes can also be torrefied at low temperatures to prepare combustible gas. Therefore, torrefaction technology can produce products with no moisture, hydrophobic solids, and increased energy density, reducing the cost of transporting and storing agricultural waste.

Torrefaction technology is now at a relatively mature stage, and the facilities for torrefaction are also being quickly developed. Commonly used types of torrefaction reactors include rotating drum reactors, fluidized bed reactors, screw-type reactors, and compact reactors. Each reactor has different characteristics, which affect the production efficiency of the target product. Among them, rotating drum reactors and screw reactors have lower heat transfer efficiency but are more flexible. Fluidized bed reactor has good heat transfer efficiency, while the size of the agricultural waste needs to be reduced to a small size to maintain the stable fluidization velocity of the reactor. So the process is very energy consuming and is not commonly used as a torrefaction reactor. In addition, torrefaction parameters (temperature, oxygen, and residence time) will also affect product quality. Firstly, different torrefaction temperatures cause changes in the calorific value, cellulose, ash, and carbon content. For example, the composition of bagasse after torrefaction at low temperatures has no significant change, but the oxygen content and cellulose of bagasse will decrease, and the carbon content will gradually increase with the gradual increase of torrefaction temperature (Kanwal et al. 2019). Sadaka and Negi (2009) also found that increased torrefaction temperature may increase the pH of the product. Secondly, different residence times can also have an impact on the quality and yield of the baked product. The mass losses of biomass are proportional to the residence time, which is mainly caused by biomass devolatilization. In addition, the carbon content of the value-added products produced by torrefaction was positively correlated with the residence time (Yoo and Choi 2016). The elemental compositions of torrefaction products are also affected by temperature and residence time. With the increase of isothermal temperature and residence time, the values of H/C and O/C will decline (Trouvé et al. 2021). During the torrefaction process, excessive oxygen can also be generated, leading to a faster devolatilization reaction. Due to the existence of oxygen content, the time required for the entire process will be shortened (Kota et al. 2022). Previous studies have also found that gas-pressurized torrefaction with different gas pressures affects the calorific value and yield of biomass. It has high carbon content, aromaticity, and smaller porosity under high gas pressure.

In general, torrefaction is a promising agricultural waste conversion technology. After torrefaction, biochar and bio-oil with high energy density and good hydrophobicity can be produced. The resource utilization of agricultural waste can also reduce environmental pollution and alleviate the energy crisis. Globally, most torrefaction technologies are already commercialized, while a few are still in the experimental stage. In view of the current problems in the torrefaction process, future research and development trends are mainly in the following aspects. Firstly, the torrefaction pretreatment process and the uniformity of temperature distribution in the heating furnace need to be further improved to produce homogeneous products. Secondly, the optimal torrefaction parameters are supposed to be explored when two or more agricultural wastes are co-mixed for torrefaction. Finally, further investigation of the reaction mechanism and kinetics of agricultural waste devolatilization and the energy consumption during the torrefaction process should be evaluated in the future.

7.2.2 Pyrolysis

Pyrolysis, as a highly evaluated biomass thermochemical conversion technology, can convert biomass into value-added products at high temperatures under anaerobic conditions (Chen et al. 2018). Pyrolysis is mainly divided into three stages (Shen et al. 2017). The first stage is the drying stage, in which the temperature rises locally, leading to water evaporation. The second stage is the primary pyrolysis stage, in which the chemical bonds in the biomass components break and decompose into the main volatile matter (CO, CH_4, and CO_2), organic matter, and water, and the temperature is relatively low (<500 °C). The final stage is secondary pyrolysis, where the temperature is high (>500 °C), that is, some major volatiles released from the biomass particles participate in various secondary reactions here and finally can generate bio-oil, biogas, and biochar. A typical diagram of a pyrolysis unit is shown in Fig. 7.2.

During the pyrolysis process, the yield and composition of the product will change as the operating conditions change. Among them, pyrolysis temperature is an extremely important influencing factor. When the pyrolysis temperature is low (300–400 °C), biomass dehydration generates less gas and bio-oil, but higher

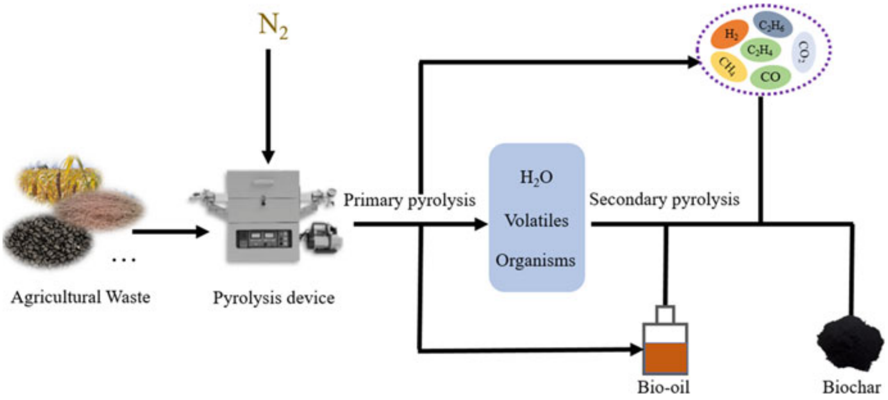

Fig. 7.2 Diagram of pyrolysis unit

biochar yield is obtained. This is because covalent bond breaking and decomposition reactions are more likely to occur in the center of biomass particles at low temperatures. When the pyrolysis temperature reaches 400–500 °C, the generated gas and bio-oil increase relative to the low temperature, and the yield of biochar decreases relative to the low temperature. At high pyrolysis temperature (550 °C), the yield of syngas increased, but the yield of biochar and bio-oil decreased significantly, due to the decomposition of cellulose and hemicellulose. It is worth mentioning that although the yield of biochar at high temperature is small, it has better physicochemical properties, such as higher specific surface area and pore volume, excellent aromatic structure, etc. At low temperature (300 °C), the longer residence time can lead to higher stability of biochar. However, at high temperature (600 °C), the effect of residence time is relatively weak (Wang et al. 2020b). Concurrently, the heating rate also plays an important role in the pyrolysis process. The yield of bio-oil will progressively rise with an increase in heating rate but will fall when the temperature of the pyrolysis process is too high because of the pyrolysis reaction of volatile materials at high temperatures. Moreover, increasing the heating rate is conducive to the formation of CO and CH_4, and the yield of biochar has also been improved (Chen et al. 2016). To sum up, the impact of the pyrolysis process is multifaceted, and it is necessary to fully consider the impact of various operating parameters to explore the best operating parameters.

Good control of the above operating conditions can produce high-quality pyrolysis products, which can be better used in practice. Therefore, the application of pyrolysis products of agricultural wastes will be introduced one by one. Bio-oil contains aromatic hydrocarbons, tar, methanol, acetic acid, etc. Its components are complex and cannot be directly used as fuel. Distillation is a common method for purifying bio-oil, which can extract useful chemicals from bio-oil. However, since bio-oil has weak thermal stability, a polymerization reaction may occur when distilling at atmospheric pressure, which is not conducive to the separation of bio-oil components. It has been shown that distillation at high pressure reduces polymerization reactions, resulting in high distillate yields, thanks to the high-pressure retaining water and other light components in the liquid phase to reduce the degree of polymerization (Wang et al. 2021). Another highly efficient bio-oil treatment technology is hydrogenation technology, which is considered one of the most promising ways to produce renewable fuels and chemicals. In short, the technology hydrogenates the unstable components of the bio-oil at lower temperatures and then heats the partially treated bio-oil to higher temperatures, thus meeting the more complete deoxidation required to produce the hydrocarbon containing fuel.

The composition of syngas generated from the pyrolysis of agricultural wastes is usually complex, mainly including CO, CO_2, H_2, CH_4, and N_2. To realize the efficient utilization of syngas, it can be further transformed into value-added chemicals. For example, syngas can be used to synthesize methanol. Methanol synthesized from syngas generated from biomass pyrolysis has lower H_2 and higher CO_2 content (Adil et al. 2022). Syngas can also be used to synthesize formaldehyde ether, which is a typical diesel additive. It is miscible with diesel oil to reduce toxic and harmful gases emitted during combustion. It has been found that when formaldehyde ether is added to diesel fuel, greenhouse gas emissions are reduced by nearly 20%, and soot emissions are also reduced by 30% (Mahbub et al. 2017).

As the most important value-added product of biomass thermochemical conversion, biochar is more widely used than bio-oil and syngas. With rich functional groups, large specific surface area, and porosity, biochar has been widely used in carbon fixation, soil improvement, and pollution control. The surface of biochar is rich in charge, which has a strong electrostatic attraction to pollutants with specific charge types. In addition, the application of biochar in the field of catalysis is also worth mentioning. Its application in the field of advanced oxidation has received extensive attention in recent years, including its combination with periodate, Fenton, and persulfate. Therefore, the products from biomass pyrolysis have considerable application prospects and are of positive significance for promoting sustainable development.

However, biomass pyrolysis technology still has some shortcomings at this stage (Chen et al. 2018). First of all, the biomass raw materials are diverse, and further research on the pyrolysis process of different raw materials is needed. Secondly, some more advanced technologies such as pyrolysis gas chromatography mass spectrometry (Py-GC/MS) should be used to study the properties of pyrolysis products and the pyrolysis process. To achieve higher pyrolysis efficiency, the development of a continuous reactor with higher pyrolysis temperature and shorter residence time to replace fixed bed reactor has been an important development direction of biomass pyrolysis technology. Finally, for the sake of data reliability, pilot analysis beyond laboratory-scale experiments should be strengthened.

7.2.3 Gasification

Gasification is a thermal conversion process, consisting mainly of drying, pyrolysis, coke gasification, and combustion stages. Organic or fossil fuel-based carbonaceous materials can be converted into low to medium calorific value gaseous products through gasification. In the gasification process of agricultural waste, some tar is formed through the recombination of primary and secondary pyrolysis products. Some research results show that temperature has the greatest effect on tar release, while residence time and different air/fuel equivalent ratios have the least effect (Briesemeister et al. 2017). In recent years, gasification technology has also been applied to the recycling of agricultural wastes. Gasification allows agricultural waste to be converted into gaseous products or combustible gases at high temperatures, which can then be used directly as fuels or intermediates in the synthesis of chemicals, such as syngas, kerosene, hydrogen, etc.

The gasification process involves various complex reactions and can be divided into four stages, namely, drying, pyrolysis, oxidation, and reduction (Salem and Paul 2018) (Fig. 7.3). Firstly, the water in agricultural waste is dried at 100–150 °C and removed as water vapor. Secondly, agricultural waste is first decomposed into volatiles and char after drying. Then, the waste is converted into condensable gases, tar, and char during pyrolysis in the presence of limited oxygen. Furthermore, the oxidation zone increases the heat required for drying and pyrolysis of agricultural waste, and the various oxidative chemical reactions during the gasification process release the heat needed for endothermic reactions here. Finally, endothermic reactions occur in the reduction zone and a large amount of syngas is produced.

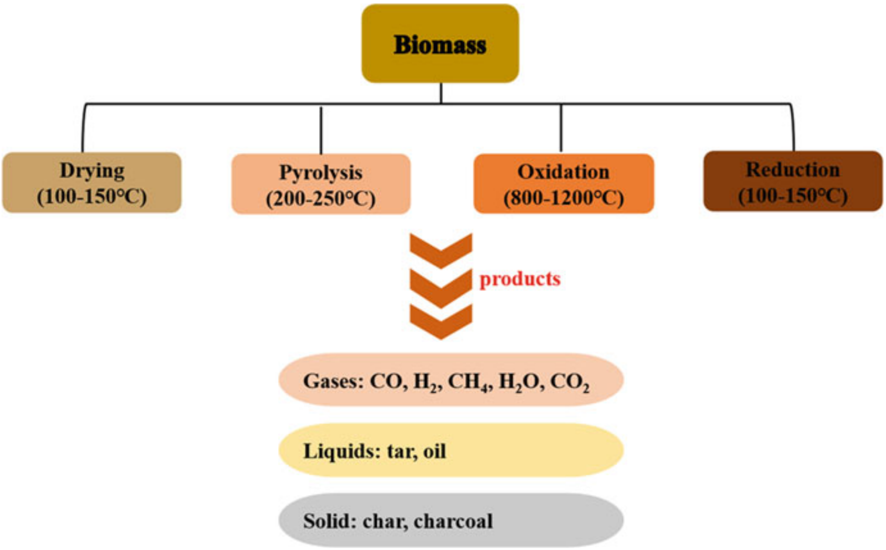

Fig. 7.3 Gasification process and product

Appropriate catalysts can reduce the economic cost of the gasification process. Among them, dolomite has the advantages of availability, low cost, and simple treatment, which is a kind of gasification catalyst with high potential. The tar can be completely removed by raising the dolomite temperature to 800 °C via steam induction (Shahbaz et al. 2017). The temperature is proportional to the feed of the gasification medium, and the endothermic reaction can be promoted with the increases of temperature. Gasification medium also has a positive effect on process efficiency and can improve the yield and quality of products. Commonly used gasification media are air, oxygen, steam, carbon dioxide, and supercritical water, because air is rich in sources and is the most commonly used gasification medium.

Gasification is the process of converting waste into syngas. Syngas is one of the main products of biomass gasification and can be regarded as an energy carrier for a variety of applications. It is one of the main sources of environmentally friendly fuels and chemicals. At the same time, it can also be used in electricity production. The gasification process can be classified from the aspects of gasification medium, heating source, gasifier design, and process pressure. According to the different gasification media, it can be divided into air gasification, steam gasification, oxygen gasification, and combined gasification process. The heating source can be divided into plasma process direct heating and indirect heating. According to the different designs of the gasifier, it can be divided into circulating bed, bulged fluidized bed, fixed bed, fluidized bed, etc. Based on process pressure, it can be divided into atmospheric gasification and high-pressure/pressurized gasification (Sajid et al. 2022).

As a typical gasification method, steam gasification can be used to produce H_2, and the technology has been well developed. During the cooling process, the syngas produces high-quality steam, which can be gasified and reformed with char and tar to convert syngas into CO and H_2, or water gas, to maximize efficiency. However, in the process of steam gasification, if the tar is not effectively separated, the production and quality of the gas will be affected, so the tar needs to be cleaned at a high temperature before the gas can be utilized (i.e., hot gas cleanup). The hot gas purification process can use a plasma torch to crack tar and can also treat tar through multiple gasification methods, such as pyrolysis gasification integration (Sikarwar et al. 2016). Special processes have also been developed to convert different types of biomass into usable gas or electricity. Toxic organic waste can be vaporized by plasma, which can be produced by heating gas or exposing the substance to a strong electromagnetic field. Plasma can be used as a heat source during gasification or for tar cracking after standard gasification. At present, plasma gasification is mainly used to decompose toxic organic wastes, rubber and plastics, and other hazardous biomass wastes. Wet biomass can be converted using supercritical water gasification (SCWG). Supercritical water is water that is between liquid and gas phases and above the critical point ($T = 647$ K and $P = 221$ bar) (Schienbein and Marx 2020). SCWG has been applied to wet biomass without the need for pre-drying. The product gases produced by SCWG mainly include H_2, CO_2, CH_4, and CO, among which H_2 is the main component of the gas produced. Because the product gas component is dissolved quickly in supercritical water, the formation of tar and char is also relatively reduced.

Although gasification has been widely used to convert agricultural waste into biofuel, it still has some drawbacks. For example, up to 40% of the biomass raw materials are burned with oxygen in the air in the gasifier, which will inevitably cause a large amount of waste of biomass raw materials. In addition, biomass combustion products such as CO_2 may pollute syngas, thus reducing the quality of syngas and affecting their use. The utilization rate of products after the gasification of different agricultural wastes is also different. For example, in agricultural processing plants and fields, nonwoody biomass is a common waste material. It has a large volume and relatively low energy, and nonwoody materials from agricultural wastes are very cheap and abundant. Compared with woody biomass, the energy production efficiency of nonwoody biomass is relatively low. To reduce tar production and improve syngas production efficiency, nonwoody biomass can be co-gasification by mixing with catalysts (e.g., dolomite, CaO, etc.) or high-quality solid fuels (e.g., coal) (Widjaya et al. 2018). Therefore, the potential application and future development direction of nonwood gasification are worthy of further discussion. The products obtained from gasification using agricultural wastes as raw materials have gradually become substitutes for fossil fuels, which can not only save costs but also reduce dependence on fossil resources and regulate greenhouse gas emissions. However, biofuels or chemicals produced from agricultural waste are still in the laboratory stage, and their commercial production and utilization are still in the initial stage, requiring further research and exploration. Biomass gasification appears to be more suitable for commercialization than other biomass thermochemical transformation technologies, especially in the field of thermochemical transformation technologies for generating renewable fuels. However, the production cost of syngas is still prohibitive for many people. Therefore, as a potentially sustainable and environmentally friendly technology, gasification needs further research and exploration to expand its commercial application.

7.2.4 Hydrothermal Carbonization

The pyrolysis technology mentioned above can produce rich products with high added value through thermochemical conversion, but one of its disadvantages is that the source of raw materials is limited. Biomass for thermochemical conversion through pyrolysis can only be dry biomass, which requires strict requirements. Therefore, researchers have developed another thermochemical conversion method, namely, hydrothermal carbonization (HTC). At low temperature or moderate water conditions, hydrothermal carbonization is a sustainable method for transforming biopolymers or other biomass into high value-added products like carbon-containing compounds (Adolfsson et al. 2020). It is controlled by hydrolysis. During hydrolysis, cellulose, hemicellulose, and lignin are decomposed into small fragments, so as to dehydrate and decarboxylate to reduce H/C and O/C ratios (Heidari et al. 2019). This method does not need to dry biomass, which greatly saves energy. Currently,

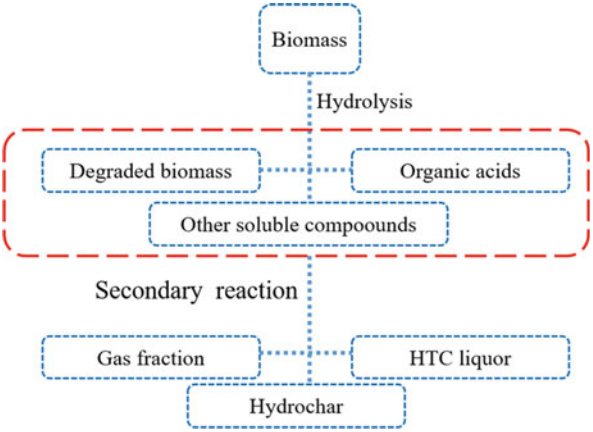

Fig. 7.4 Working principle of hydrothermal carbonization technology

hydrothermal carbonization (HTC) is considered to be one of the most common approaches for transforming biomass into high value-added products. The working principle of this technology is shown in Fig. 7.4.

Compared with pyrolysis, hydrothermal reaction conditions are more moderate (180–150 °C) and its carbon dioxide emissions are less. The products with a high added value obtained from hydrothermal carbonization are very rich, and the typical one is hydrothermal carbon, which is widely used in soil remediation, energy storage, adsorbent, catalysis, and other fields (Nakason et al. 2018). Hydrothermal carbon can be used as a potential energy source in the future world. From the current situation, the focus of the field of agricultural wastes transforming into hydrothermal carbon through hydrothermal carbonization gradually tends to the hydrothermal carbonization of combined raw materials (CO-HTC). This approach can enhance the yield, physicochemical properties, and overall quality of hydrothermal carbon, while also improving environmental issues to some extent, as waste utilization is increased. Furfural can be used as a bactericide, perfume, and refinery lubricant recovery, while 5-HMF is often used to produce fine chemicals and plastics (Borrero-López et al. 2017). Research shows that sludge can produce clean biofuels, organic fertilizers, and precursors of functional materials through hydrothermal carbonization (Wang et al. 2019). However, as the chemical composition of different biomass raw materials varies greatly, attention should be paid to their safety and potential risks when using them.

Although this method is technically feasible, it may not be so good from an economic perspective. Compared with the current market price of coal, it is still at a disadvantage (González-Arias et al. 2022). In addition, the future hydrothermal carbonization of biomass should further develop improved integrated processes to benefit from various stages of the process. Finally, the new commercial configuration of this technology needs to be introduced to the market, and the purpose of energy optimization needs to be achieved, but it still has a long way to go. In conclusion, the heat treatment method of biomass hydrothermal carbonization has great application prospects and broad development space.

7.3 Advanced Thermochemical Processes

7.3.1 Use of Microwave

The previous section briefly introduced how torrefaction, pyrolysis, gasification, and hydrothermal carbonization technologies make agricultural wastes into value-added end products. In response to the disadvantages of these techniques, such as low yields, long reaction times, and high energy consumption, researchers have also applied some auxiliary methods to overcome the above shortcomings, including microwave-assisted and electrochemical-assisted pyrolysis, etc. Among them, the method of pyrolysis of solid biomass containing lignocellulose to obtain bio-oil using microwaves was proposed by Allan and colleagues (Richel and Jacquet 2015). Numerous studies have shown that microwaves have advantages in terms of yield, reaction time, and reduced reaction temperature in the conversion process of agricultural waste. According to available information, the application of microwaves in thermochemical conversion is mainly concentrated in pyrolysis and hydrothermal carbonization processes. In the conventional pyrolysis process, heat is transferred from the outside to the inside of biomass, resulting in uneven heating. In contrast, microwave-assisted pyrolysis (Fig. 7.5) (Zhao et al. 2012) involves microwave passing through the interior of the biomass and causing the internal molecules to vibrate, the interior to be heated first and then gradually diffused to the exterior of the biomass. In addition, the use of electrochemical-assisted pyrolysis mainly accelerates the pyrolysis process of biomass through catalysts. Therefore, the thermal uniformity of heat in the whole process is better improved by microwave-assisted pyrolysis, and the energy consumption is reduced. The process of microwave pyrolysis of agricultural waste includes free water evaporation, primary decomposition (dehydration, demethylation, and decarboxylation), and biopolymerization and pyrolysis of bio-oil (Lin et al. 2021). Besides, the combination of microwave and hydrothermal carbonization mainly heats the raw materials

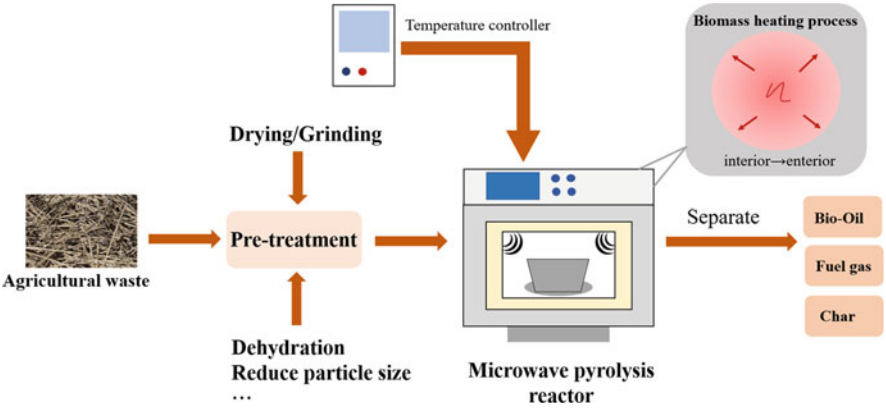

Fig. 7.5 Microwave-assisted biomass pyrolysis process

from inside through dielectric heating phenomena such as dipole polarization or ion conduction. Many waste peels and livestock manure can be microwave-assisted hydrothermal carbonization to improve their yield in the preparation of hydrochar (Wang et al. 2020a). Compared with traditional hydrothermal carbonization, microwave-assisted hydrothermal carbonization makes the raw materials more uniformly heated, quickly reaching the hydrothermal carbonization equilibrium, reducing the loss of organic components, energy consumption, and processing time. At the same time, the performance of the fuel produced by microwave-assisted hydrothermal carbonization has also been significantly improved.

During assisted pyrolysis/hydrothermal carbonization, different microwave power will affect the conversion efficiency and product performance. According to the literature, when the microwave power increases within a certain range, the content of H_2 and CH_4 in rice straw also increases correspondingly (Huang et al. 2010). When the microwave power changes from 400 to 800 W, the percentage of gas output of wheat straw increases by 67%, and the percentage of CO and CH_4 changes the least (Zhao et al. 2014). Therefore, in terms of product yield, the gas yield increases with microwave power, while the solid yield is the opposite. In terms of product performance, microwave pyrolysis/hydrothermal carbonization increases the carbon content of the product, reduces the hydrogen and oxygen content, and improves thermal stability. In addition, the H_2 generated during microwave-assisted pyrolysis process can also be used to synthesize methanol, natural gas, biomethane, etc. The remaining gas products can also be used in the pyrolysis system to reduce the energy consumption of the pyrolysis process (Fodah et al. 2022). The operation mode of microwave pyrolysis is divided into two types: intermittent and continuous. Intermittent microwave pyrolysis is the most common mode of operation, which increases the reaction residence time, affects the homogeneous reaction, has low pyrolysis efficiency, and damages the quality of pyrolysis products (Fan et al. 2021). To improve the efficiency of pyrolysis and achieve continuous production of pyrolysis products, continuous microwave pyrolysis technology was developed (Luo et al. 2021). The mechanism of continuous microwave pyrolysis is that the feedstock in the fixed-bed reactor is heated to the target temperature under stable microwave output power, followed by periodic heating to maintain a relatively stable. The organic components of the feedstock absorb microwave energy and destroy the main backbone of the organic macromolecules, forming carbon chain radicals, followed by the formation of coagulable and non-coagulable products (Fodah et al. 2022).

At present, microwave-assisted pyrolysis/hydrothermal carbonization is considered to be a promising technology, but its practical application is still a great challenge. Firstly, microwave heating of agricultural waste is safe within the laboratory, but there are still potential risks associated with scaling up microwave heating due to exposure to microwave radiation. Secondly, the penetration depth of microwaves is limited, and the low selectivity of the desired product as well as the variability of the dielectric properties of different agricultural wastes can affect the yield. Finally, further research is still needed on how to fabricate suitable reactors and design pyrolysis systems to improve the output and quality of value-added end products.

7.3.2 Integrated Biochemical and Thermochemical Processes

To better solve the problem of energy crisis and waste accumulation, thermochemical and biochemical conversion methods can be used to produce bioenergy. Agricultural waste can be effectively transformed into biological products and bioenergy with high use value through thermochemical processes. The biochemical transformation of biomass is carried out through the activity of microorganisms, resulting in the production of hydrogen, ethanol, methane, and biodiesel, among other products, through hydrolysis, fermentation, enzymatic synthesis, and photosynthesis. Biofuels are one of the most effective ways to reduce transport emissions and dependence on fossil fuels, and biofuels derived from biomass could significantly reduce the production of CO_2. Agricultural waste is being converted into biochar, bio-oil and syngas, and other advanced energy products through thermochemical conversion techniques. This can improve their calorific value and fuel characteristics, and the use of agricultural waste such as bagasse and oat husks benefits the biofuel sector.

At present, the high consumption and high cost of natural gas urge people to look for alternative energy for green economy. Hydrogen production from biomass provides such an alternative. The production of biohydrogen ($BioH_2$) from agricultural waste is a relatively green process, as its synthesis is completed under low temperatures and lower pressure conditions. The production of $BioH_2$ from agricultural waste is economically and environmentally feasible, which has attracted wide attention worldwide. There are four methods for biological hydrogen production: The production of $BioH_2$ by dark fermentation is a natural process in an anaerobic environment. $BioH_2$ can be produced by light fermentation with the help of anaerobic microorganisms under the condition of light energy. The production of $BioH_2$ by light and dark fermentation can increase its yield, which is caused by the sequence of light and dark fermentation microorganisms. $BioH_2$ is produced by microbial electrolytic cells (Kumar Sharma et al. 2022).

Although biochemical conversion technology has been developed for more than 70 years, its operation process still has more limitations than thermochemical conversion technologies. Moreover, the biochemical method to produce $BioH_2$ is more expensive than the thermochemical method. The growth conditions need to be carefully controlled during the biological treatment. Therefore, researchers are more inclined to develop thermochemical methods for $BioH_2$ production, such as gasification and pyrolysis technology. SCWG of biomass is considered to be an economical thermochemical method for hydrogen production, which is extremely advantageous for reducing the formation of char and tar. In the process of pyrolysis, biomass is converted into steam, tar, and char. The production of hydrogen through pyrolysis will be affected by the formation of tar, which will reduce the hydrogen content. Therefore, appropriate catalysts should be used to minimize the formation of tar, such as CaO. In the process of thermochemical transformation, inorganic substances can be produced, which have different degrees of influence on the transformation process. For example, inorganic matter plays a catalytic role, changing the thermal degradation rate, bio-oil yield, etc. During combustion in the pyrolysis process, inorganic substances pose environmental risks and may have health effects, as well as technical problems. In the process of gasification, the inorganic matter will bring diversified harm to the downstream area. Therefore, it is necessary to adopt a series of pretreatment and posttreatment technologies to control and reduce the influence of inorganic substances in the transformation process. Pretreatment technologies include mechanical, thermal, and chemical pretreatment, which can reduce pollution concentration limits by removing inorganic contaminants. The posttreatment technologies include the posttreatment of gas products and liquid products, which are mainly used to meet the cleaning requirements of downstream areas. At the same time, these treatments also have some disadvantages, such as more chemicals generated after pretreatment and higher facility and drying costs.

Considering the practical application of thermochemical transformation technology, many studies have evaluated the environmental performance of biofuels produced by thermochemical transformation. Alcazar-Ruiz et al. (2022) studied the full life cycle assessment to compare the environmental performance of two thermochemical processes: gasification and rapid pyrolysis, that is, the thermochemical treatment of different types of agricultural waste to obtain bio-oil. Because both processes have very high CO_2 emissions, comparisons with different agricultural biomass allow for the identification of biomass types and thermochemical processes that have the least impact on the environment. This study is novel in comparing these two thermochemical processes. The gasification products can be used in a Fischer-Tropsch reactor to obtain high-quality bio-oil, while the operating conditions of the rapid pyrolysis process can promote the conversion of lignocellulosic biomass into useful forms of energy (mainly bio-oil). Studies have also been conducted to convert dried cow dung at an average temperature of 320 °C and balm leaf biomass fuel into biochar by thermochemical transformation, which has higher pore volume and smaller pore size. Therefore, we should carefully explore the thermochemical transformation technology of biomass, as well as the corresponding life cycle assessment of the environmental impact and socio-economic performance of the final product. The thermochemical transformation of biomass is applied to the iron and steel industry, which takes place below 1000 °C, and steel making takes place above 1200 °C. Therefore, waste heat can be recovered in the process of steelmaking and it is feasible. The use of alternative biomass fuels in the iron and steel industry can reduce greenhouse gas emissions to a certain extent. It is reported that the use of biomass can reduce 0.8 tons of CO_2 emissions per ton of metal, that is, reducing greenhouse gas emissions by 58% (Suopajärvi et al. 2014).

Combining biochemical transformation with thermochemical transformation can make up for the limitations of biochemical transformation. It can also transform waste biomass which is difficult to biodegrade into value-added products. Cellulosic ethanol can be produced from lignocellulose, such as corn straw and wood chips, but the pretreatment of lignocellulose often requires strict conditions such as high temperature and pressure, so a large amount of energy is consumed (Zhu and Pan 2010). In this case, thermochemical methods used to produce biofuels can be complemented by biological pretreatment to reduce energy consumption. For example, processing cellulose waste using physical refining generates waste that is

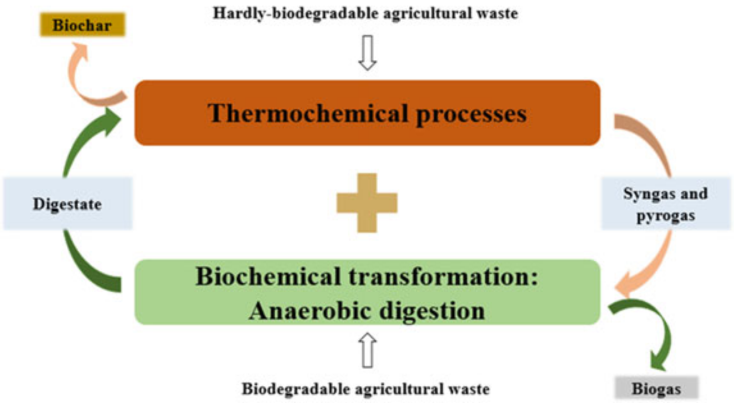

Fig. 7.6 A dual system of thermochemical technology and biochemical transformation

extremely energy-consuming compared to biomass treated with thermochemical pretreatment. Cellulosic waste, especially sulfite pulp mill waste, can be converted to ethanol efficiently through a combination of physical refining and quasi-synchronous enzymatic saccharification. A large amount of ethanol production can make up for the problem of energy consumption (Wang et al. 2013). This shows that combining bioprocessing with thermochemical methods can reduce energy consumption while improving energy efficiency. In addition, some researchers have combined anaerobic digestion with gasification to improve the conversion efficiency of raw agricultural waste (Antoniou et al. 2019). Although anaerobic digestion solves part of the problem of energy and material recovery, the purpose of waste recovery is not fully achieved because a large part of organic matter is still preserved in the "digestion." In the gasification process, materials can be transformed through high temperatures, so the infiltration of the gasification process and anaerobic digestion in the dual system can better improve the recovery of energy and materials. In addition, the dual system can effectively reduce the generation of secondary waste. Anaerobic digestion and gasification are coupled in a cascade manner, and the output of anaerobic digestion is the input material for the gasification process (Fig. 7.6). The dual system can not only exist independently but also be incorporated into the regional model of circular economy. When used as a standalone dual system, it can manage agricultural waste, reduce waste landfills, and convert digestion from biogas plants into products such as energy for plant consumption or char for agriculture.

Combining thermochemistry and biotransformation into a unified process can also well optimize the remaining fiber products in the biotransformation process and use them as raw materials for thermochemical transformation. Improving the efficiency of biomass transformation and the yield of converted products and integrating the two transformation methods into a unified process can promote energy balance compared to using one method alone. However, this integration is still in its infancy.

The existing research is limited and many mechanisms remain undiscovered. Further research is highly needed to promote its large-scale use.

7.4 Conclusions and Perspectives

This chapter discusses the necessity of thermochemical conversion of agricultural waste. The advantages and disadvantages of the current agricultural waste thermochemical transformation technologies and their applications are summarized. At present, the thermochemical transformation technologies of agricultural waste are mainly divided into roasting, pyrolysis, gasification, and hydrothermal carbonization. The reaction conditions of each method are different, and the raw material requirements are also different, so it is necessary to make a judgment based on the actual situation. These thermal transformation technologies are widely used in fuel, adsorbents, energy carriers, and other fields. Thermochemical conversion technology can convert agricultural waste (a renewable carbon source) into solid, liquid, and gaseous fuels. Therefore, in the field of energy recovery, agricultural waste has very good development potential. In addition, with the continuous advancement of research, some auxiliary processes of biomass thermochemical transformation can also be well applied to the high-value utilization of biomass, such as microwave-assisted pyrolysis and biochemical transformation technology combined with microorganisms. However, there is still a long way to go in this aspect, which is one of the main future research directions.

The thermochemical transformation of agricultural waste is a very promising way to produce alternative energy sources. The coordination of biomass pretreatment, catalyst, and thermochemical conversion transformation can be better applied to large-scale treatment or the actual production of high-quality end products. The complexity of biomass structure can be reduced by optimizing chemical, biological, roasting, and other pretreatment technologies. In future research, it is necessary to select appropriate pretreatment technology and catalyst to improve the quality of required products. However, pretreatment techniques can remove some inorganic substances, increase the volume or density of biomass, and possibly add chemicals, resulting in an increase of operating costs. Therefore, the posttreatment technology used after thermochemical conversion needs to be considered, which can meet the strict cleaning requirements in downstream applications. At the same time, because the conversion process requires high temperature and high pressure, this will increase its operating costs. In future research, we should also focus on making full use of waste heat to minimize costs.

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Advances in Thermochemical Valorization of Agricultural Waste

8

Nitin Kumar and Sunil Kumar Gupta

Abstract

Globally, a huge amount of agricultural waste is generated from different sources such as agronomy, livestock management, and other allied agricultural activities. Inappropriate disposal and management of agricultural wastes negatively affect the environment and remains a cause of legitimate concern for the government and environmentalists. This waste is commonly rich in nutrients, lignocellulosic material, etc. and possesses high potential to be transformed into valuable assets such biochar, bio-oil, bio-crude, biofertilizers, syngas, enzymes, organic acids, etc. The studies revealed that if agriculture waste is managed in a sustainable way, it could prove to be a treasure contributing toward circular economy. This chapter describe an overview of various thermochemical technologies widely explored for sustainable management of agricultural waste. Critical review of different technologies demonstrated that the thermal digestion—a novel technology—seems to be a quick and environment-friendly process for converting agro-wastes into organic fertilizer.

Keywords

Agricultural waste · Thermochemical treatment · Nutrients · Waste management · Organic fertilizer

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8.1 Introduction

Agriculture is one of the largest economic sectors, which generate enormous amount of waste from various agro-based operations. Annually, around 140 billion tons of agricultural waste (AW) are generated globally (Dey et al. 2021). India, being an agro-based country, generates about 657 million tons (Mt) of crop residue annually that is expected to rise up to 868 Mt. by 2030 (Tagade et al. 2021). In most of the developing countries, a huge amount of AW is still either openly dumped or incinerated in the barren land. This improper practice for the management of AW led to serious environmental concerns such as emissions of greenhouse gases, health hazards, and soil degradation (Rahimi et al. 2022). Hence, the proper management and disposal of these wastes always remain a matter of legitimate concern for the government, stakeholders, and the environmentalists.

The optimal management and utilization of AW could open a new window for the production of sustainable resources, contributing toward energy security, ecological sustainability and development, and conservation of resources, and promote circular economy (Awogbemi and Von Kallon 2022). This requires conversion of agro-waste into valuable resources such as composts, biochar, adsorbents, and organic fertilizers using state-of-the-art technologies. Researcher and scientist explored different types of physical, chemical, and biological processes for transforming this waste into useful end products. Among them, biological treatment is recognized as green technology for the transformation of organic residue into biofuels without any adverse impact to the environment. However, due to the presence of lignocellulosic material, which is highly recalcitrant to biodegradation and requirement of intensive time, it makes this process reluctant. Therefore, under the umbrella of the circular economy, innovative technologies and novel approaches are being explored for the recovery of resources from AW.

Thermochemical conversion pathways, which require less time and environmental footprints, are getting popularity for transformation and extraction of valuable products from waste. The advanced thermochemical technologies included pyrolysis, gasification, hydrothermal liquification, incineration, and thermal digestion, for the recovery of biochar, syn-gas, bio-crude, and nutrients from AW. These technologies contributed immensely to ensure the sustainable transformation of wastes into valuable products together with reducing the adverse environmental impacts (El-Ramady et al. 2020). This chapter presented an overview of the waste generation, its composition, and characterization together with various technological approaches of thermochemical conversion processes explicitly used for converting AW into valuable resources.

8.1.1 Sources and Composition of Agricultural Waste

The agricultural sector of India has witnessed paradigm shift in terms of mechanized farming, cropping system, fertilizer usage, optimal irrigation, etc. The agricultural activities in India cover about 60% of the total land area (~156.4 Mha) (Tagade et al.

Table 8.1 Classification of various type of agricultural waste and their residues

Source of major agricultural waste	Crops	Primary residue	Secondary residue	References
Cereals	Rice	Straw, leaves, stubble	Husk	Singh et al. (2021)
	Wheat	Straw, leaves, stubble	Pod	
	Sorghum	Straw, leaves	Bagasse	
	Maize	Stalks	Cob	
Sugar processing	Sugarcane	Top steam, leaves	Bagasse	Chowdhury et al. (2018)
Fibers	Cotton	Stalk	Seeds, gin	Tagade et al. (2021)
	Jute	Stalk, leaves	Caddies	
Oil extraction	Sunflower	Stalks, leaves	Cake, husk	Chowdhury et al. (2018)
	Soybean	Stalks, leaves	–	
	Mustard	Stalks, leaves	Cake, husks	
	Castor	Stalks, leaves	Cake, husks	
	Palm	Stalks, fronds	Shell	
Miscellaneous	Banana	Leaves, stems	Fruit peel, piths	Tagade et al. (2021)
	Coconut	Leaves, branches	Shells, coir piths	
	Groundnut	Stalks	Shells	

2021). With the boom in agricultural sector, the generation of crop residue increased appreciably. However, out of the total generated waste, only 20–30% is utilized either for feeding animals or energy production (Rahimi et al. 2022). Different types of agricultural crops generate various types of residues, which primarily depends on climatic conditions, geographical location, and soil properties. Generally, the agro-residues are categorized into two main categories, that is, primary and secondary residues (Table 8.1). Primary residues are generated during harvesting of the crops such as straws, stalks, branches, leaves, etc. Secondary residues are those that are generated during the processing of agricultural products, which mainly include cobs, cakes, husks, shells, etc. (Tagade et al. 2021). Total AW generated from the major cropping in India is shown in Fig. 8.1. The majority of total agro-based residue is composed of cereals, sugarcanes, fibers, and oilseed-based waste. Cereal crops are mainly harvested from October to November, whereas sugarcane is harvested from October to May, and their residues contribute about 360 Mt. (56%) and 145 Mt. (22%), respectively. In contrast, fiber crops are mainly harvested in from January to February, whereas oilseed crops are harvested from March to April, and their residues contribute 66 Mt. (10%) and 59 Mt. (9%), respectively (Bagwari and Todaria 2011; Sukumaran et al. 2017).

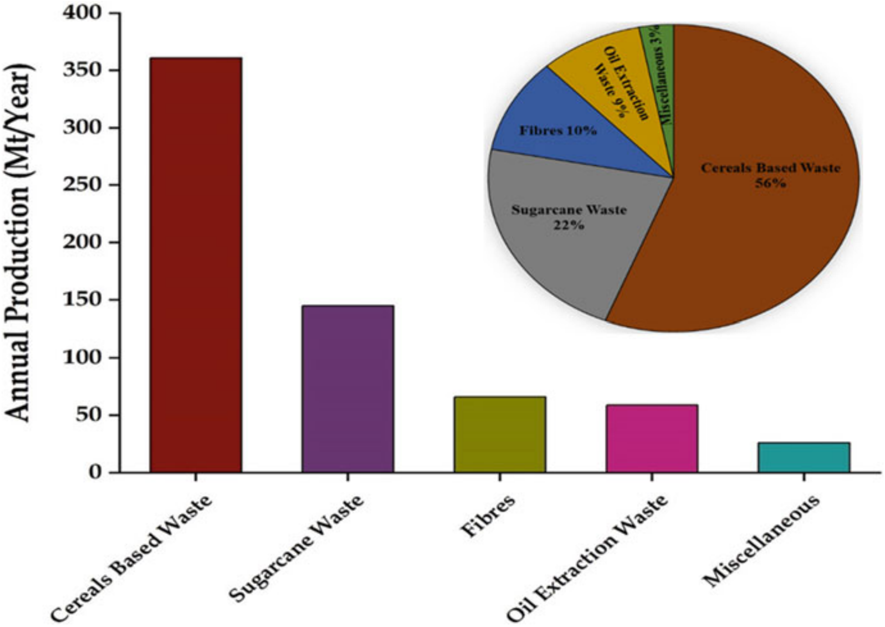

Fig. 8.1 Quantification and fractionation of various types of agricultural wastes generated in India

8.1.2 Characterization of Various Types of Agricultural Waste

Proper categorization of different AW is requisite to clearly understand their physicochemical characteristics to facilitate efficient management, optimal processing, and recovering value-added resources through various conversion routes. The analysis of proximate, ultimate, and lignocellulosic composition of AW provides significant information for selecting the most suitable conversion technique. However, different AW has different composition, which ultimately depends upon the topographical location and the conditions under which the crops are grown and cultivated. The physicochemical characteristics of different agro-residue is presented in Table 8.2.

Principal components of an agro-waste include lignin (21–40%), cellulose (25–44%), and hemicellulose (10–40%). On the basis of percentage of lignin, it could further be classified into three classes, namely, low lignin (<10%), medium lignin (10–20%), and high lignin (>20%) (Ge et al. 2021). Agro residues such as coconut shells, sugarcane tops and leaves, rice husk, groundnut shells, etc. have low lignin content. Straw of wheat and rice, coconut coir, sugarcane bagasse, and maize stems have medium lignin content. And banana pseudo-stem, mustard stalks, sesame press cake, and soybean husk have high lignin content. AW is also found rich in nitrogen (~0.5%), phosphorus (~0.2%), and potassium (~1.5%), which could be recycled to provide nutrients to intensify the crop yield. In general, the AW has low moisture content (<15%), which makes it suitable for processing through

Table 8.2 Physicochemical characteristics of various types of agro-residue

Agro-waste	*Physicochemical characteristics (%)*[a]										
	MC	VM	Ash	C	H	N	S	O	Lignin	Cellulose	Hemi cellulose
Sugarcane bagasse	13–16.5	70–84	2–3	44–52	5.3–5.8	0.3–0.4	0.03–0.05	42.5–47	12–18	38–45	25–32
Rice husk	6–8	71–81	20–24	35.5–39	3.8–5.2	0.6–0.8	0.04–0.06	32–36	26–35	32–40	19–25
Rice straw	5–7	75–80	6–15	37–44	5.0–6.8	0.4–1.3	0.21–0.26	38–42	19–26	38–46	26–34
Wheat straw	6–8.5	63–78	2–13	42–46	5.0–6.2	0.2–0.4	0.04–0.06	38–46	18–25	35–40	32–38
Groundnut shell	5–8.5	79–83	6–10	48–52	5.4–5.9	0.6–1.2	0.5–0.8	44.5–48	25–35	36–42	16–24
Corn straw	5–7	73–78	5.5–9	43–48	5.6–6.0	0.4–0.6	0.8–1.2	46.5–50	10–18	40–48	22–28
Coconut shell	10–12	75–80	0.8–3	48–52	5.7–6.5	0.2–0.7	0.4–0.6	38–45.5	26–32	18–26	50–58
Cotton stalk	4.5–7	74–79	6.5–8	40–44	6.0–6.4	0.4–0.7	0.4–0.5	42.5–48	28–36	39–47	22–38
Corn Stover	11–14	79–83	3.5–5	43–47	5.0–5.6	0.5–0.8	0.06–0.1	36.5–40	18–24	34–45	26–34
Mustard press cake	10.5–15	66–72	6.5–8	41–45	7.0–7.7	5.8–7.2	0.5–0.9	44–47.5	16–28	45–54	24–32
Banana pseudo-stem	8–14	86–90	9–11	32–36	6.1–6.7	0.6–1.2	0.04–0.08	47.5–51	15–25	25–36	22–30
Sunflower shell	3.5–5	81–84	4.5–6	48–50	5.5–6.1	0.4–0.8	0.3–0.5	39–42.5	17–24	45–52	32–40
Tea waste	6.5–8	82–87	1.5–4	48.5–51	5.2–5.9	0.3	0.1–0.4	40–44.5	38–46	32–38	21–28

[a] Compiled from: Alhazmi and Loy 2021; Tagade et al. 2021; Rahimi et al. 2022

thermochemical treatment. However, property of the generated biochar, bio-oil, and syngas is significantly influenced by the high volatile and low moisture content of the AW (Rahimi et al. 2022).

8.2 Existing Thermochemical Conversion Technologies

Thermochemical conversion is considered as one of the most suitable technology for transforming agricultural biomass into useful resources despite the requirement of high energy input (Ong et al. 2019). These processes yield higher quantity of end product in comparatively shorter reaction time. Thermochemical treatment involves high temperature chemical dissociation that involves breaking of bonds and conversion of organics into biochar (solid), bio-fuel (liquid), and syngas (Rahimi et al. 2022). Some of the important thermochemical conversion methods commonly applied for the treatment of AW is shown in Fig. 8.2.

8.2.1 Pyrolysis/Torrefaction

Torrefaction is relatively a mild thermal conversion technique that is executed at a lower temperature (200–300 °C) in the presence of an anoxic atmosphere resulting in the production of solid fuel with higher hydrophobicity and lower concentration of O_2 (Alhazmi and Loy 2021). Pyrolysis is different from torrefaction in terms of operating temperature, as pyrolysis is performed at higher temperatures (around 300–800 °C), which involves thermal degradation of biomass in an inert atmosphere resulting into complete removal of volatile, yielding useful end products such as biochar, volatile gases, and bio-oil (Chew et al. 2021). Schematic layout of the pyrolysis process for agricultural waste is shown in Fig. 8.3. Among various routes of thermochemical processing, pyrolysis has emerged as one of the most

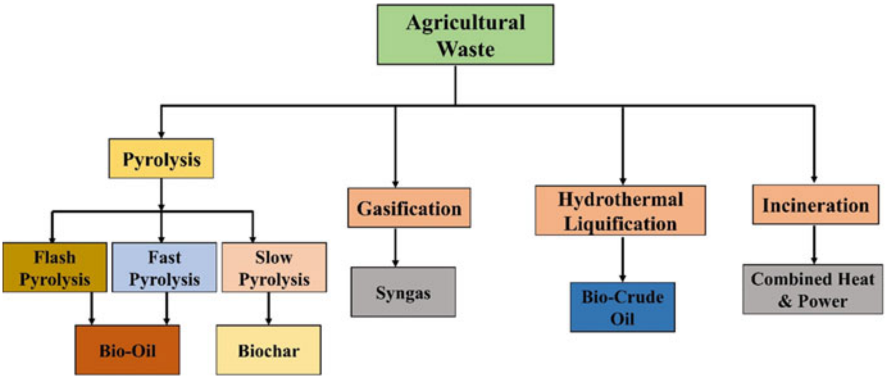

Fig. 8.2 Thermochemical pathways for transformation of agricultural waste into value added end products

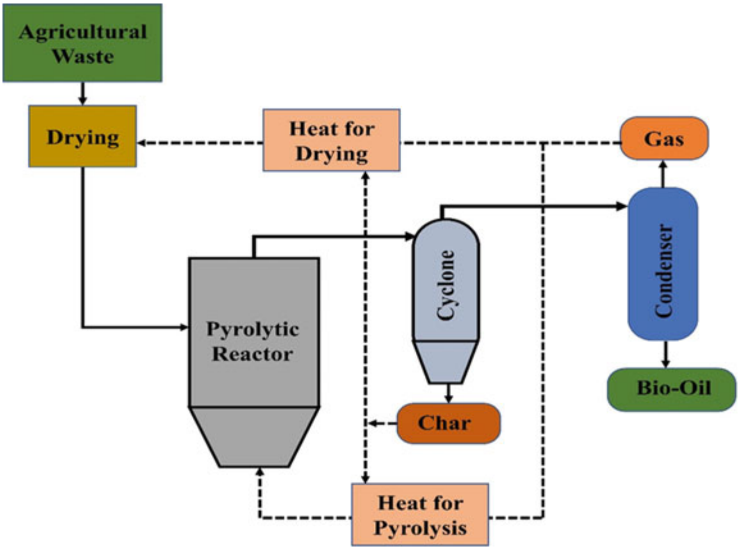

Fig. 8.3 Schematic layout of the pyrolysis process for agricultural waste

environment-friendly and cost-effective process because of its flexibility to transform biomass into different forms of energy. The char is refined to produce adsorbents for the removal of heavy metals and various pollutants from water, wastewater, and soil. The bio-oil could be utilized as a fuel, whereas the gas is internally recycled for heat generation. Based on input temperature, heating rate, and vapor residence time, pyrolysis is typically classified into three categories: slow, fast, and flash pyrolysis (Singh et al. 2021).

Pyrolysis of various agricultural waste and their major end product is summarized in Table 8.3. In slow pyrolysis, repolymerization process occurs that maximizes the yield of solid residue, that is, biochar. This process involves the thermal breaking of bonds at moderately lower temperature (~400 °C) and higher vapor residence time (Lee et al. 2019). The desired product of slow pyrolysis is a solid residue, that is, biochar; however, both liquid and gaseous products are also generated, but generally, these are not recovered. The solid product, that is, biochar obtained from this process, could effectively be utilized as soil amendments, adsorbents for water and wastewater treatment, and carbon nanotubes. Fast pyrolysis is performed at higher temperature (~500 °C), by providing a higher heating rate ($> 200\ ^\circ\mathrm{C\ s^{-1}}$), and shorter vapor residence time (0.5–15 s), which yields bio-oil (Lee et al. 2019). The obtained bio-oil could effectively be utilized as a fuel to generate energy. Moreover, bio-oil comprises of various additional components that could be sequestrated and reutilized as feedstock for food, fertilizer, and pharmaceutical industries. Flash pyrolysis is carried out at a much higher temperature (450–1000 °C), by providing a heating rate up to $700\ ^\circ\mathrm{C\ s^{-1}}$, and much shorter vapor residence time (< 0.5 s) that favors the yield of higher amount of bio-oil (up to 80%) (Patel et al. 2020). Gases

Table 8.3 Pyrolysis of various agricultural waste and their major end product

Type of substrate	Process	Type of reactor	Experimental condition	Major end product	References
Rice husk	Slow pyrolysis	Fixed bed	Temperature: 400 °C; nitrogen flow rate:10 L min^{-1}	Biochar: 49.5%	Alhinai et al. (2018)
Sugar cane bagasse	Slow pyrolysis	Fixed bed	Temperature: 420 °C; Heating rate: 21.3 °C min^{-1}	Biochar: 32.6%	Carrier et al. (2011)
Olive kernels	Fast pyrolysis	Fixed bed	Temperature: 600 °C; gas residence time: 0.4 s Flow rate of carriergas: 0.20 mL min^{-1}	Bio-oil: 63.2%	Volpe et al. (2018)
Corncob	Fast pyrolysis	Fluidized bed	Temperature: 500 °C; Gas residence time: 1 - 2 s	Bio-oil: 41%	Yanik et al. (2007)
Palm kernel shell	Flash pyrolysis	Fluidized bed	Temperature: 600 °C; flow rate of feed gas: 5 L min^{-1}	Bio-oil: 73.74%	Maliutina et al. (2017)
Pinewood sawdust	Flash pyrolysis	Conical spouted bed	Temperature: 500 °C; nitrogen flow rate:30 L min^{-1}	Bio-oil: 77%	Amutio et al. (2011)

generated from the pyrolysis process, that is, the pyro gas, are a combination of CH_4, CO, C_6H_6, H_2, and CO_2 that could be internally recycled as fuel for power generation (Tagade et al. 2021).

8.2.2 Gasification

Gasification of AW is performed at high temperature (700–1400 °C) and varying pressure (0.1–3.3 MPa) under the presence of oxidizing agent (Lee et al. 2019). Flow diagram of a gasification process used for agricultural waste is shown in Fig. 8.4. This process involves the use of gasifying agents, such as oxygen/air and steam, to transform the biomass into combustible gas (syngas) (Ong et al. 2019). This process results in the conversion of biomass into syngas consisting of H_2 (18–20%); CH_4 (2–3%); CO (18–20%); CO_2 (8–10%); a fraction of H_2O, N_2, and light hydrocarbons; and various other contaminants such as ash char, oils, and tars. Moreover, the process conditions for the gasification could be modified to generate syngas of desired quality that is utilized for electricity generation or used as a raw material for manufacturing methanol, ammonia, gasoline, etc.

When gasification is done with air as an oxidizing agent, the equivalence ratio (ER) is considered as the most significant variable, which is defined as the ratio of actual air supplied/kg of fuel as per the stoichiometry. Basically, the ER determines the part of fuel, which is burned and gasified inside reactor (Natarajan and Baskara Sethupathy 2015). The progression of gasification could be considered as direct or

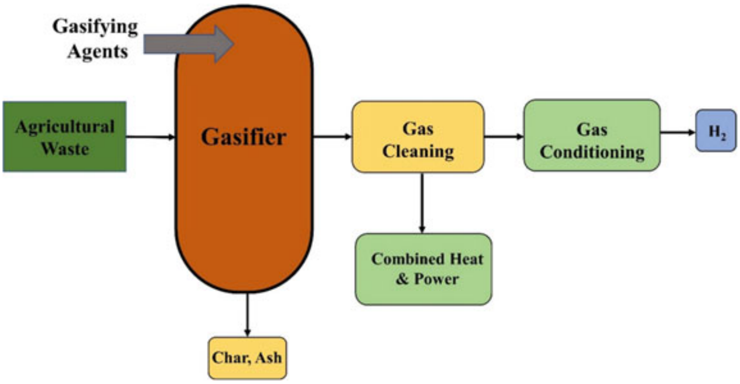

Fig. 8.4 Flow diagram of a gasification process used for agricultural waste

indirect. The former requires a gasification agent and an additional source of energy. And the latter occurs when the feedstock gets partially oxidized to sustain desired level of temperature. The general objective of gasification is to maximize the production of syngas and minimize the production of condensable hydrocarbons and unreacted chars.

Temperature and reaction time of the process could significantly be decreased using Ni-based catalysts and alkali earth metals (Ong et al. 2019). The composition and characteristics of produced syngas is significantly affected by the type of gasifier, gasifying agent, and catalyst used. Gasification of various agricultural waste and the corresponding heating value of the syngas is summarized in Table 8.4. Gasification is considered a better option for the treatment of AW in terms of energy efficiency and higher heat capacity. Moreover, this process could be customized into a continuous system for simultaneously converting the syngas into other enzymes and bio-chemicals (Alhazmi and Loy 2021). In comparison to the other thermochemical conversion techniques, gasification is associated with the greater flexibility of the feedstock material and minimal hazardous emissions (Awasthi et al. 2021).

8.2.3 Hydrothermal Treatment

Hydrothermal liquefaction (HTL) of biomass is an innovative technique in which mainly liquid fuel, that is, bio-crude is produced along with various other solid, aqueous, and gaseous by products. Schematic diagram of hydrothermal process used for agricultural waste is shown in Fig. 8.5. HTL is mainly carried out in a reactor operating at a medium temperature (250–400 °C) and high pressure (5–30 MPa) in the presence of water or a mixture of organic solvent and water (Isa et al. 2018). At a high temperature, water act as a catalyst and reactant that transforms the organic matter by attaching hydrogen ions to the hydrocarbons.

Table 8.4 Gasification of various agricultural wastes and heating value of the derived syngas

Type of substrate	Type of reactor	Experimental condition	Heating value of the syngas	References
Groundnut shells	Fluidized-bed gasifier	Temperature: 800 °C; ER: 0.30; particle size: 1 mm	4.13 MJ Nm^{-3}	Natarajan and Baskara Sethupathy (2015)
Olive kernels	Fixed-bed gasifier	Temperature: 950 °C; ER: 0.3 Gasifying agent: Air	8.60 MJ Nm^{-3}	Awasthi et al. (2021)
Rice husk	Fluidized-bed gasifier	Temperature: 735 °C; ER: 0.3	3.76 MJ Nm^{-3}	Makwana et al. (2015)
Sugarcane bagasse	Downdraft biomass gasifier	Temperature: 850 °C; ER: 0.22	5.4 MJ Nm^{-3}	Awais et al. (2021)
Rice straw	Downdraft-bed gasifier	Temperature: 800 °C; ER: 0.3; addition of 2% iron-based catalyst	18.0 MJ Nm^{-3}	Chiang et al. (2016)
Coconut shells	Downdraft biomass gasifier	Temperature: 785 °C; ER: 0.29	6 MJ Nm^{-3}	Awais et al. (2021)
Rice husk	Downdraft-bed gasifier	Temperature: 900 °C; ER: 0.3	5.19 MJ Nm^{-3}	Murugan and Sekhar (2017)

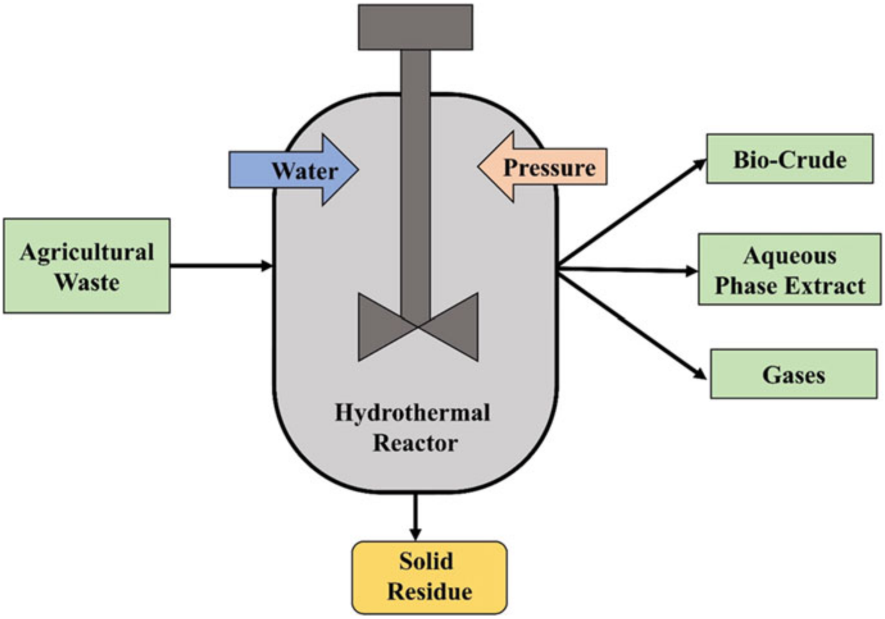

Fig. 8.5 Schematic diagram of hydrothermal process used for agricultural waste

Table 8.5 Process parameters for hydrothermal liquification of agricultural wastes

Type of substrate	Type of reactor	Operating conditions	Heating value of the bio-crude	References
Corn Stover	0.25 L autoclave reactor	Temperature: 375 °C, pressure: 4 MPa; retention time: 15 min	35.13 MJ kg^{-1}	Mathanker et al. (2020)
Barley straw	1 L autoclave reactor	Temperature: 300 °C; pressure: 9 MPa; Retention time: 15 min	24.87 MJ kg^{-1}	Zhu et al. (2015)
Wheat straw	Tubular batch reactor	Temperature: 350 °C; Pressure: 20 MPa	28 MJ kg^{-1}	Patil et al. (2014)
Rice straw	0.25 L autoclave reactor	Temperature: 300 °C; retention time: 120 min; use of NiO as catalyst	31.9 MJ kg^{-1}	Younas et al. (2017)
Sorghum bagasse	0.25 L tubular reactor	Temperature: 300 °C; retention time: 60 min; Use of K_2CO_3 as catalyst;	33.1 MJ kg^{-1}	Bi et al. (2017)
Sugarcane bagasse	0.5 L autoclave reactor	Temperature: 250 °C; retention time: 15 min; Use of $MgMnO_2$ as catalyst	32.16 MJ kg^{-1}	Long et al. (2016)

Near the critical point of water (374 °C and 22 MPa), the hydrocarbons, which are hydrophobic in nature, became water-soluble due to decline in its dielectric constant and viscosity and increase in the ionic substances that enhances the catalytic activity of the reaction. Water is typically used as a solvent because of its numerous benefits, such as its normal occurrence, environmental friendliness nature, and specific properties under HTL pressure and temperature. Water is considered as an ideal solvent because it is easily available and inexpensive. Since water is utilized as a solvent, the HTL process produces a large quantity of wastewater, which makes the recycling of water necessary for cost-effectiveness and long-term operation. The biomass rich in lignocellulosic content is considered as the most suitable feedstock for the HTL process. The HTL of various agricultural wastes and their end product is summarized in Table 8.5. Depending upon the operation parameters of reactor, variety of feedstock and percentage yield of bio-crude from the AW vary from 20 to 70% (Alhazmi and Loy 2021). Since preliminary drying of biomass is not necessary in HTL process; hence, it requires less energy in comparison to the pyrolysis process. Moreover, the heating value of the bio-crudes obtained by HTL is found superior to the bio-oil obtained from pyrolysis. However, the requirement of higher operating pressures for its operation presents a challenging task for scaling up the HTL process.

8.2.4 Incineration

Incineration is the oldest and widely used technique that reduces the volume of waste up to 85% (Babu et al. 2022). Incineration involves controlled combustion of agricultural/organic waste at a temperature > 900 °C. Output from incineration comprises of release of heat, fly ash, bottom ash, and emissions into air (Bernstad and la Cour Jansen 2011). The heat generated during the process may be used to operate steam turbines and generate electricity (Panepinto et al. 2015). Also, the ash generated from the incineration could be treated and reutilized in various industries such as cement, ceramics, road construction, agriculture, etc. (Kanhar et al. 2020). In order to have effective incineration with energy recovery, the average calorific value of waste should be between 1700 and 1900 kcal kg^{-1}. The incineration process could be divided into two steps, that is, primary and secondary processes. The primary process involves drying, combustion of fixed carbon, burning, and volatilization of organics. And the secondary process involves combustion of gases, vapors, and particulate matter that are driven off during the primary process (Begum et al. 2012). Generally, incineration of one ton of MSW generates approximately 544 kWh of energy and produces 180 kg of solid residue (Zaman 2010). The mineralization of organic substances into harmless end products is one of the major advantages of the incineration process. In contrast, the release of various toxic and noxious gases (dibenzofurans, chlorinated dibenzo-p-dioxins, greenhouse gases, etc.) discouraged its application (Sharma et al. 2019). However, the use of suitable air pollution control devices could restrict the release of these gases into the atmosphere.

8.3 Advanced Thermochemical Processes

8.3.1 Use of Microwave

In microwave heating, microwave irradiation provides quick volumetric heating as it directly interacts with the inside particles of the material and converts the electromagnetic energy into heat (Fodah et al. 2022). Therefore, in comparison to the conventional process, the heat loss in the microwave method is largely avoided because of volumetric heating of the feedstock.

Microwave pyrolysis has emerged as a novel technique for converting AW into biochar, bio-fuels, and syngas. In comparison to conventional the approach, microwave-assisted pyrolysis of AW is found superior in providing higher heating rate that supports the yield of higher quantity of value-added products. Moreover, the microwave-assisted pyrolysis exhibited complete removal of the volatiles that yields biochar with cleaner surface and less cracks. Moreover, the biochar obtained from microwave pyrolysis exhibited higher reactivity because of the enhanced surface area and lower crystallinity. Microwave pyrolysis was found highly efficient in degrading hemicellulose-rich biomass at lower temperature range (200–300 °C), hence requiring minimum microwave power. The biomass rich in lignin requires higher temperature (>350 °C) for pyrolysis, which requires a higher microwave power (≥ 450 W) to increase the yield of biochar with enhanced properties (Ge et al. 2021).

In context to conventional pyrolysis, microwave pyrolysis is also found efficient in yielding higher amount of bio-oil. Higher temperatures (500–600 °C) and high power (up to 900 W) enhance the heating rate resulting into higher yield of bio-oil (Fodah et al. 2022). Moreover, bio-oil yielded from microwave pyrolysis is found enrich in carbon and low in oxygen, contributing toward higher heating value and lower susceptibility to chemical degradation. The operational conditions of microwave pyrolysis such as temperature, heating rate, reaction time, input power, type of catalyst type, and the type of feedstock extensively governs the yield of bio-oil.

A reaction temperature (>600 °C) and a microwave power (>900 W) with higher reaction time results in the yield of larger amount of syngas. The gas generated during the microwave pyrolysis is composed up of H_2, CO_2, CO, CH_4, and a trace of other elements. The fraction of these components in the produced gas varied significantly according to pyrolysis conditions and the feedstock used. The nitrogenous atmosphere is found most effective in yielding higher gas in comparison to purging of different gases such as CO, H_2, and CH_4. The use of catalysts such as activated carbon, Ni, MgO, and SiC during the microwave pyrolysis process also increases the gas yield. Despite high capital and operation costs, microwave-assisted pyrolysis of AW is considered economically viable in producing of high-quality biochar, bio-oil, and syngas (Ge et al. 2021). However, the scaling-up of the microwave-assisted technology is complex because of the possible risk associated with the exposure of microwave radiation.

8.3.2 Integrated Biochemical and Thermochemical Processes

Hybrid treatment systems combining both thermochemical and biological processes are now gaining significant attention due to their potentially higher economic and environmental benefits. The implementation of a thermochemical treatment after biochemical degradation process improves the feedstock utilization efficiency and assists in yielding higher amount of required end product. The merger of anaerobic digestion (AD) with the pyrolysis process reduces the total operational cost and makes the whole process more energy sustainable (Okolie et al. 2022). Monlau et al. (2015) recommended to reuse the dried digestate as a feedstock for pyrolysis. They found that integration of AD with pyrolysis process led to increment in electricity gain by up to 42%. A different type of an integrated system is the merger of pyrolysis with the AD process (Okolie et al. 2022). In this combined system, the biochar obtained from the pyrolysis process is added to AD plant to enhance the nutrient retention and C:N ratio and reduce the chances of nutrient leaching for efficient land application of the digestate. Torri and Fabbri (2014) studied the AD of the bio-oil obtained from the pyrolysis process and found that the addition of biochar led to a twofold increase in methane yield. The gases derived from the pyrolysis process could also be fed to the AD unit to let anaerobic microorganisms transform the pyrolytic gases into biogas to enhance the product yield.

The integration of HTL with the AD could improve the efficiency of energy generation from the biomass (Okolie et al. 2022). Through HTL process the digestate from the AD plants could be transformed into valuable aqueous fuel, that is, the biocrude. Hoffmann et al. (2013) provided an integrated design for the treatment of digestate obtained from AD of animal manure through HTL process. They found that in comparison to alone AD plant, the integrated system produced high-quality biofuel having a higher heating value (43 MJ kg^{-1}). Despite the high potential of integrated system for the thermochemical biological processes, the major bottleneck associated with these systems is the mass transfer of the gaseous substrate through the liquid medium. However, because of the robustness of the integrated system in improving the digestion efficiency of the biomass, these hybrid systems came out as an attractive approach for the production of advanced bio-products.

8.3.3 Thermal Digestion Technique

In thermal digestion process, thermal energy is directed toward the biomass to heat up the solids and rapidly eradicate the moisture content. This process is usually applied for the processing of sludge/digestate, but nowadays, it has emerged as an effective approach for the rapid conversion (within 4–6 h) of solid organic waste into a nutrient rich organic fertilizer (Kumar and Gupta 2021). In this method, the waste is shredded (into <10 mm size) and heated at a relatively lower temperature (~150 °C), which helps in digesting the organics and converting them into a simpler form. The heat is transferred uniformly to the digestion chamber through a convection mode of heat transfer. The digestion chamber is equipped with an agitator, which facilitates uniform and continuous mixing of the shredded waste to improve the drying rate. The digestion process is carried out until the waste material attains the equilibrium moisture content, that is, near nil moisture. After completion of the digestion process, the dried mass is pulverized into a powder form of uniform consistency.

During the digestion process, the value of total N is slightly reduced due to the loss of water-soluble NH_4^+-N. However, the digestion process helps in degrading the high molecular weight organic N into low molecular weight organic N and creates a dry bond N structure, which converts the waste into a slow-release fertilizer. At the same time, the organic P gets oxidized into inorganic phosphate form, while the physically bounded K gets converted into exchangeable K^+ form and thus enhances the bioavailability of P and K by converting it into plant available form (Kumar and Gupta 2022). The end product of the thermal digestion process is devoid of any pathogen and moisture; hence, it could easily be stored for longer duration without any change in its nutrient value. This method is quick, hygienic, and easy to operate and requires very small area for its operation, making it suitable for the treatment of agricultural waste. The comparison of the thermal digestion process with the existing thermochemical techniques in terms of operational parameters and their end products is summarized in Table 8.6.

Table 8.6 Evaluation of thermal digestion technique versus other thermochemical techniques

Technology	Parameters				End product
	Temperature (°C)	Working atmosphere	Operating pressure	Treatment duration (h)	
Pyrolysis	300–800	Anoxic	Atmospheric	2–4	Biochar, bio-oil, CO_2, CO, CH_4
Gasification	500–900	Oxygen limited	Atmospheric	1–2	Syngas and ash
Hydrothermal treatment	150–250	Oxygen rich	Autogenic	8–10	Bio-oil, hydrocar, CO_2, H_2
Incineration	>900	Oxygen rich	Atmospheric	4–8	Fly and bottom ash, gaseous emissions
Thermal digestion	150	Oxygen rich	Atmospheric	4–6	Organic fertilizer

8.4 Summary and Conclusions

This chapter presented an overview of sources, quantification, and characterization of AW and explored various thermochemical conversion processes widely explored for converting AW into value added products. The slow pyrolysis is considered suitable to obtain higher yield of biochar, while the fast and flash pyrolysis yields greater amount of bio-oil. And gasification and HTL process are mainly used to recover syngas and bio-crude, respectively. Microwave-assisted pyrolysis of AW was found superior over conventional pyrolysis by providing higher yields of value-added products. Nowadays, the hybrid systems combining the operation of both thermochemical and biological treatments are gaining considerable attention due to the potential ecological and economic advantages. However, commercial level scaling-up of these technologies still remains a challenging task due to various operational related constraints and cost economics. In this context, thermal digestion of AW seems to be a promising technology that obviates the limitations and constraints of the conventional process for the recycling of nutrients back into agricultural fields.

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9

Conversion of Agricultural Waste with Variable Lignocellulosic Characteristics into Biochar and Its Application

Manimegalai Ambayieram and Mathava Kumar

Abstract

The rapid population growth has increased the need for food and the development of the agriculture sector. Agricultural activities generate significant quantities of waste that adversely affect the ecosystem. Agricultural waste is a material whose economic value exceeds collection, transportation, and processing costs. Agricultural wastes have distinct characteristics, and researchers have focused on upgrading them into valuable products through physical, chemical, or biological treatments. Biochar production from lignocellulosic biomass through the physicochemical process finds wide application for environmental remediation. The practical usage of biochar has reduced greenhouse-gas emissions and global warming, enriched soil nutrient, and acted as energy storage material. The lignocellulosic properties of the plant biomass vary with soil conditions, climatic conditions, species, and other environmental factors. The formation of pores in biochar depends on the chemical characteristics of biomass. The preparation of biochar for the appropriate function firmly depends on the nature of the production methods. This chapter deals with distinctive agricultural wastes, their impact on the environment, and the significance of lignocellulosic characteristics for the synthesis of biochar. It emphasizes the available techniques like pyrolysis, methane production, and composting to direct agricultural waste residues into the circular economy. The preparation of biochar through the thermal process is examined to understand its application on the environment. This overview may focus on improving and commercializing biochar technology to fulfil global energy needs.

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Keywords

Agricultural waste · Lignocellulosic biomass · Biochar · Characterization · Treatment methods

9.1 Introduction

The world's population has risen from 3.7 billion in 1970 to 7.9 billion in 2021, and it may reach 9 billion by 2050 and 11 billion by 2100 (Koul et al. 2022). Due to an increase in population, urbanization, and industrialization, there has been a continuous increase in food requirements and consumption. There is a demand for developing the agriculture sector and sustainable waste management to meet the requirements. Both dynamic and advanced countries have enacted policies and have allocated considerable resources to address waste generation and disposal issues. The global waste generation was about 2.02 billion tons in 2016 and has been estimated to become 2.59 billion tons in 2030 and 3.4 billion tons in 2050 (Awogbemi and von Kallon 2022). Every year, India produces bulk solid waste, of which agricultural waste remains at the top with approximately 350–990 Mt/year. Succeeding China, India is the world's second-largest producer of agricultural waste, accounting for approximately 130 million tons of paddy straw, half of which is used as cattle fodder. In contrast, the rest is destroyed by open burning (Koul et al. 2022).

Agricultural wastes are generated during various agricultural activities such as the preparation, production, storage, processing, and consumption of agricultural products, livestock, and their products. Agricultural waste is categorized into field and process wastes. Field waste is a residue from crop harvesting, including stalks, leaf stems, and seed pods. In contrast, process waste is generated until valuable resources, including straw, stems, husks, bagasse, stalk shell peels, and roots, are produced (Fig. 9.1). The end product of the agricultural materials generated during the production and processing of agricultural materials may possess materials that can benefit humans in many ways (Obi et al. 2016).

Agricultural biomass is a significant renewable energy source, accounting for approximately 10% of the world's dominant energy inventory. Agricultural waste from crops is rich in carbon and animal manure in nitrogen sources, which can contribute to bioenergy. Most abundantly available agricultural residues like groundnut shell, coconut shell and husk, rice and wheat straw, sugarcane bagasse, and corncob are rich in cellulose and lignin (Trninic et al. 2016), which are either dumped or burned in the open environment creating pollution in soil, air, and water. Instead, the rich lignocellulosic biomass can be pyrolyzed to produce biochar, bio-oil and syngas, which finds application in soil reclamation and biofuels. The biochar can be produced by the conventional heating method, microwave method, co-precipitation, and calcination processes. The biochar showed excellent adsorption capacity for heavy metals and contaminants removal from water, wastewater, and air and helps in carbon sequestration. Besides, the biochar carbon showed increased capacitance and electrical conductivity of the electrodes used in supercapacitors (Gupta et al. 2015).

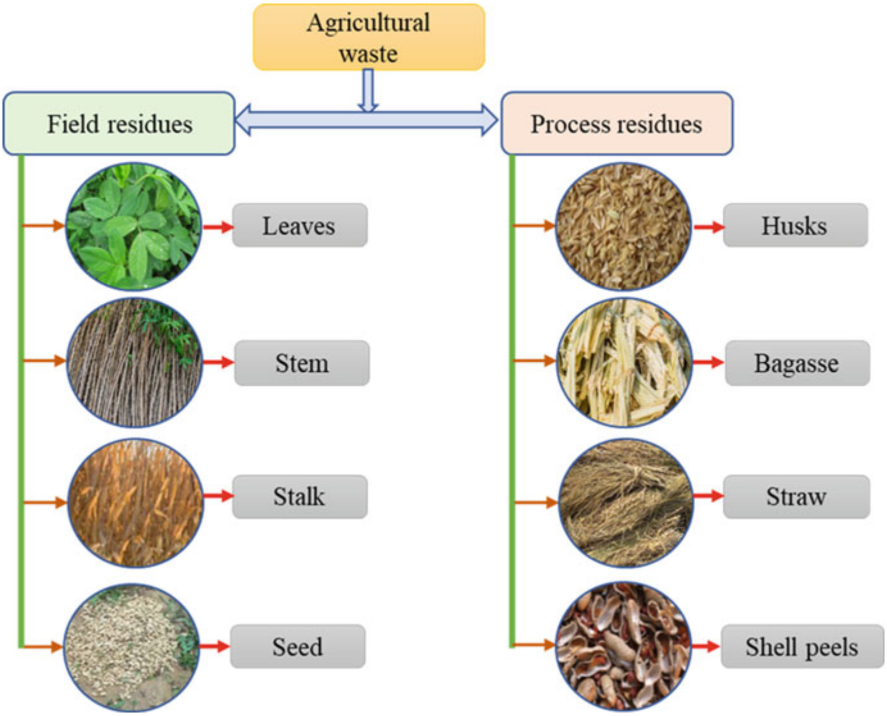

Fig. 9.1 Classification of agricultural waste

This chapter deals with agricultural waste generation, lignocellulosic composition, and its variations according to various parameters. It discusses the available treatment methods for agricultural waste depending on its characteristics. Carbonation of agricultural waste with or without activating agents results in the production of biochar and characterization techniques of biochar and their intended application in the environment.

9.2 Agriculture Waste Generation Phases

9.2.1 Pre-harvesting Phase

Pre-harvesting involves preparing the land before cultivation, and as a result, the production of solid wastes occurs. From clearing the land to harvesting crops, waste is generated at each stage of agricultural activities. At this stage, waste is generated before crop maturity, and the seed moisture content during harvest is 35–45%. If the moisture content exceeds the optimum content in the field before harvest time and the seed starts to germinate, therefore, drying to the optimum moisture content for harvesting and storage is safer. In Iran, 25% of wheat cultivation is converted into waste, accounting for 54.9 kg ha^{-1} (Asadi et al. 2010). The essential factors involved during the pre-harvest stage include temperature, relative humidity, atmosphere modification, cooling, and recommended use of chemicals for insects and pests. The management of preharvest is to harvest better quality crops cultivated.

9.2.2 Harvesting Phase

During the harvesting of cultivated crops from the field, various crop residues are generated like rice straws, wheat straws, stalks, seeds, leaves, stems, etc. In India, about 16% of crops are wasted during harvest. For example, wheat has a cutter stage (0.5–2%), thresher grain stage (0.5–1%), separator process (0.04–0.2%), and other factors (Asadi et al. 2010). In India, different types of waste occur during the harvest of paddy fields due to shattering, shedding of grains, improper methods, and harvest time. Wastage is prone to more hand harvesting, which has a higher hand than hand harvesting using a modified reaper. The losses are reduced by 6.49% for cutting efficiency and 6.49% (Mishra and Satapathy 2021). Wastage in potatoes falls under two classes: Undersized potatoes that remain unharvested and poor quality potatoes that are rejected after harvest due to anomalies in size, shape and quality. The average yield was 23 t ha^{-1}, and approximately 9% (loss 1) of non-harvested potatoes were generated during harvest.

9.2.3 Post-harvesting Phase

Post-harvest loss indicates the quantity and quality of food lost during the post-harvest period. The system has related activities of crop processing, marketing, and food preparation for the final disposal of food (Kiaya 2014). The post-harvest components influencing the loss before reaching the consumer are sorting, grading, storage, handling, and transportation. After wheat harvest, the seeds must be dried and cleaned to remove inert matter, wide varieties, and diseased, damaged, and deteriorated seeds. In India, about 40% of fruit and vegetable loss occurs at the retail and consumer level as post-harvest loss. Wheat wastes post harvest comes from four categories of wastes such as transportation wastes (5.5%), winnowing wastes (0.2%), silo (store) wastes (4%), and transformation wastes (Asadi et al. 2010). In India, the post-harvest loss for paddy and sugarcane accounts for 5–15% and 10%, respectively (Ge et al. 2023).

9.3 Environmental Impacts of Agricultural Waste

In developing countries, agriculture is the primary source of domestic waste generation and produces waste at every stage of agricultural activities. Social-ecological factors influence agricultural activities, such as natural, human, and seminatural factors. Agriculture practices provide services in enhancing biodiversity, maintaining soil health, absorption of CO_2, and water availability (Fusco et al. 2023). Agricultural wastes include wastes generated during various agricultural activities, manure, and other wastes from farms that enter the water and air. Salts from silt and soil were drained from the field, and the farmers are unaware how to manage the farm waste effectively (Nagendran 2011). As a result, floods occur due to the blockage of drainage by the solid waste of agriculture. Over the past 35 years, agricultural production has doubled, resulting in a 6.87 fold and 3.48 fold increase in usage of nitrogen and phosphorus, respectively (Tilman 1999). Intensive cultivation techniques in agriculture have various environmental impacts associated with pesticides, nitrogen compounds, farm livestock waste, and soil erosion. These impacts affect animals, plants, humans, and their economic status (Skinner et al. 1997). In 2004, a study was carried out to determine the phosphorus flow (AgiPhosFA) in agricultural systems in China and its impacts on humans. It was found that phosphorus inflow and outflow in the agriculture field were 28.9 and 14.2 kg ha^{-1} a^{-1}, respectively. Hence, the average phosphorus uptake by the crops was 45.7%, and a certain quantity of inflow P accumulated as soil P caused the deterioration of water quality (Chen et al. 2008).

9.3.1 Water Pollution

It is well known that agriculture is the largest user of freshwater resources (i.e., 70% of all surface water globally), which causes depletion in fresh water and reduces water quality (Nagendran 2011). Due to the extensive application of nitrogen and phosphorus fertilizers, runoff reaches freshwater and marine water, resulting in significant impacts (eutrophication). Aquatic eutrophication causes loss of biodiversity, emergence of nuisance species, disturbance in the food chain, and destruction of fisheries (Tilman 1999). The EPA showed the presence of 46 pesticides in groundwater and 76 in surface water bodies with atrazine being the frequently found compound. Atrazine is an herbicide found mainly in 1993–1995 in the surface waters of central and north-western New South Wales. Only 10–30% of applied pesticides reach the target, and the remaining 50–75% reach the environment. The pesticide primarily found in the water was endosulfan because of its wide use in irrigation, cotton production and oilseed crops. The other pesticides include pronofos, dimethoate, chlordane, diuron, prometryn, and fluometuron (Arias-Estévez et al. 2008).

9.3.2 Air Pollution

Air pollution can be defined as the presence of toxic chemical compounds in the atmospheric air that may affect animals, vegetation, buildings, and humans. Pollutants are released directly or indirectly into the atmosphere through natural and anthropogenic activities (Ukaogo et al. 2020). Air pollution from agricultural activities is minimal, and is primarily because of machinery operations and the burning of agro-wastes (Nagendran 2011). The burning of agro-waste results in the generation of pollutants; emission of greenhouse gases; generation of aerosols such as N_2O, CH_4, CO, and NO_x particles; and a massive loss of microbial populations and soil nutrients (Gupta et al. 2022). In the presence of sunlight, these primary pollutants form secondary pollutants such as ozone, nitric acid, and nitrogen dioxide (Sabiiti 2011). Nitrogen is more mobile than phosphorus in the soil because soil bacteria convert ammonia to nitrate and nitrite, which are readily leached from the soil. Denitrifying bacteria convert nitrate to nitrous oxide, the prime greenhouse gas. Therefore, nitrate which is supplied as fertilizer and formed due to bacterial degradation, resulting in a greenhouse gas effect that causes ozone depletion and contributes to acid precipitation (Tilman 1999).

9.3.3 Soil Pollution

Soil is the collection of natural matter including the part of the Earth's surface that can support plant growth. This material results from the disintegration and decomposition of the parent material by physical, chemical, and biological means (Cachada et al. 2017). Agricultural crop production relies on the soil as a nutrient resource; however, excessive cultivation and monoculture deplete soil nutrients. Continuous depletion was noted for N, P, K, Ca, and Mg and low soil organic carbon. Plant supplement nutrients are applied in the form of fertilizers, plant residues, animals (manure), and human waste (biosolids) (Artiola et al. 2019). The use of pesticides has increased worldwide by 2000,000 t/year (47.5% herbicides, 29.5% insecticides, 17.5% fungicides, and 5.5% others) (Cachada et al. 2017). Heavy metal concentrations in the dumpsite, roadside, and agricultural soils were studied in Varanasi, which showed the presence of Cd, Mn, SO_4^{2-}, NO_3^-, and PO_4^{3-}. The high Cd and Mn values in the soil resulted from their presence in agrochemicals, such as phosphatic fertilizer, organic fertilizer, nitrogen fertilizers, and certain pesticides and germicides (Singh et al. 2015). Pesticides are semi-volatile, volatilize from the soil into the atmosphere, and are transported by the airstream to other places, generating new contaminant sites in soil, water, and air. They interfere with the dwelling of microorganisms as they are interdependent with the habitat. Enzymatic activity and the amount of hormones microorganisms produce indicate soil quality. The applied pesticides, herbicides, insecticides, and fungicides disturb biochemical pathways and deplete biotic ecosystems (Wołejko et al. 2020).

9.4 Legal Rules and Regulation of Agricultural Wastes

Policy mediation plays a crucial role in maintaining the sustainable development of the ecosystem and circular economy, as it can achieve zero carbon emissions by 2050 (Kapoor et al. 2020). The multidimensional value of resources that extends to political, social, environmental, economic, and technical domains must be supported by policies and operational decision-making based on evidence (Atinkut et al. 2020).

Table 9.1 Act and policy in different countries related to agricultural waste management

Country	Act/policy	Statement	References
USA	EPA (Environmental Protection Agency 1970)	• Deals with solid waste management, air pollution, and water hygiene • Responsible for maintaining the environmental quality to reduce pollution transferral • Control agricultural pollution	Loeh (1974)
USA	Federal Water Pollution Control Act (PL 92-500), 1972	• Reduction of agricultural pollution • Identification of non-point sources, including runoff • Source control	
Europe	Intergovernmental Panel on Climate Change (IPCC) and United Nations Framework Convention on Climate Change (UNFCC)	• Combustion of fossil fuels, agriculture, and fossil- fuel contributes to greenhouse emission	Marmo (2008)
Europe	Directive 99/31/EC	• Forbids illegal burying of plastics waste	Briassoulis et al. (2013)
	Directive 2000/76/EC	• Uncontrolled burning of plastic waste is prohibited	
	Directive 2008/98/EC	• Forbids uncontrolled discarding of plastic waste	
India	The Rashtriya Krishi Vikas Yojana (RKVY), 2007	• Agro-waste bioconversion and bio-compost production	Bhuvaneshwari et al. (2019)
India	Integrated Agricultural Waste Management (IAWM)	• Reduction of waste production • Reduce, reuse, and recycling policies • Waste the new products (like methane) • Sustainable solution	Choudhary et al. (2018)
United Nations (44 countries)	Food and Agricultural Organization, 1945	To reduce poverty and improve the living standard of the world's population	Duque-Acevedo et al. (2020)
India	FICCI, 2018	• Focus on biogas technologies in small and large-scale	Kapoor et al. (2020)
India	• As per section 144 of the Civil Procedure Code (CPC)—The Air Prevention and Control of Pollution Act • The Environment Protection Act 1986 • The National Tribunal Act	To ban the burning of agricultural waste	Bhuvaneshwari et al. (2019)

(continued)

Table 9.1 (continued)

Country	Act/policy	Statement	References
	1995 • The National Environment Appellate Authority Act 1997		
India	The New National Biogas and Organic Manure Programme (NNBOMP) under the Ministry of New and Renewable Energy (MNRE)	• Clean cooking fuel for households, small power needs for farmers • Replacement chemical fertilizer with slurry from the biogas plant	Kapoor et al. (2020)
Europe	Erntekunststoffe Recycling Deutschaland (ERDE), 2016	• National recovery program in Germany, which recovers plastic films	Green (2019)
	Cicloagro scheme	• Tax on the sale of agricultural plastics and authorization to collect nonpackaging agriculture plastics in Andalusia	
	Agriculteurs Distributeurs Indudtriels pour la VALORisation des dechets agricoles (ADIVALOR)	• Scheme set up by manufacturers, distributors, and farmers that deal with packaging, plastic film, and pesticide waste	

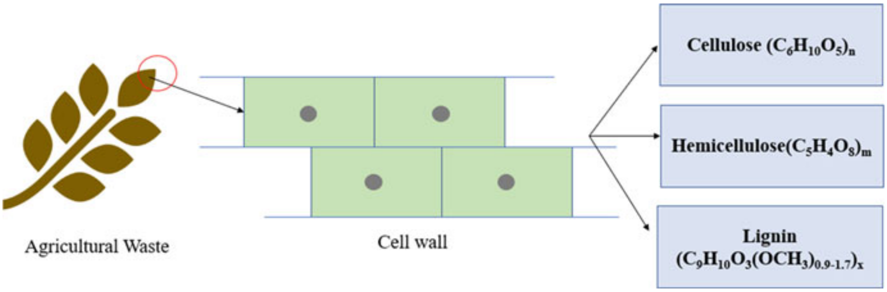

Fig. 9.2 Lignocellulosic composition of cell wall

Table 9.1 lists some acts and policies related to agricultural waste management in different countries.

9.5 Elements of Lignocellulosic Composition

Determination of the chemical composition of lignocellulose is vital for its potential use in the industry (Gismatulina et al. 2022), as shown in Fig. 9.2.

9.5.1 Cellulose $(C_6H_{10}O_5)_n$

Cellulose comprises homopolymer sugar units with a linear chain of several hundred to tens of thousands D-glucose units. B-1,4 glycosidic bonds with hydrogen bonds interlink them, and van der Waals forces hold for 40–50% of the cellulose molecules in plant biomass (Alawad and Ibrahim 2022). The insoluble crystalline cellulose (I) polysaccharide structure can be transformed into other polymers (II, III, and IV) by treatment. Enzymes can hydrolyze transformed polymers (Zhao et al. 2012).

9.5.2 Hemicellulose $(C_5H_4O_8)_m$

Hemicellulose is a branched short-chain heteropolymer with 50–3000 sugar units in cellulose fibers, linking microfibrils with non-covalent bonds. Polymers are composed of hexoses (β-D-mannose, β-D-glucose, and α-galactose), pentoses (β-D-xylose and α-L-arabinose), and uronic acids (α-D-glucuronic and α-D-4-*O*-methyl-galacturonic-D-galacturonic) (Bandgar et al. 2022). A covalent bond connects lignin and hemicellulose; the principal hemicelluloses found in grass and straw are arabinan, galactan, and xylan. Mannan is found in Harwood and softwood. Hemicellulose hydrolysis is easier than cellulose because few hydrogen bonds are involved in bonding (Nahak et al. 2022).

9.5.3 Lignin $(C_9H_{10}O_3(OCH_3)_{0.9-1.7})_x$

Lignin accounts for 10–25% of the total mass of the plant's biomass composition, mostly phenyl-propane polymers, which are commonly linked by ether bonds and form bulk polymers with long chains of building blocks (Nahak et al. 2022). Lignin is an amorphous polymer that confines cellulose and hemicellulose and acts as a waterproofing agent and protector against microorganisms and insects (Alawad and Ibrahim 2022). The phenylpropane units used were sinapyl alcohol (syringyl propanol), coumaryl alcohol (*p*-hydroxyphenyl propanol), and coniferyl alcohol (guaiacyl propanol). Hardwood has guaiacyl propanol as the building block, whereas softwood contains coniferyl and sinapyl alcohol as the primary building blocks. Lignin impedes the deterioration of cellulose during hydrolysis. Lignin is neither hydrolyzed nor fermented (Ashokkumar et al. 2022).

9.6 Parameters Influencing Biomass Composition

9.6.1 Soil Type and Geographical Location

Various environmental factors, such as weather, amount and period of water supply, temperature variation, and differences in local soil conditions (clay, sand, rock, nutrient content, and pH), influence plant biomass composition (Williams et al.

2016). Certain combinations of physicochemical and biological factors are required to maintain soil strength. The spatial variability of soil properties is controlled by inherent variations in soil characteristics (e.g., parental material, vegetation, and climate) or is affected by exogenous factors, such as crop production practices (tillage, fertilization, and crop rotation) (Valliammai et al. 2021). A study was conducted at seven sites spanning a variety of soils within Illinois with *M. giganteus,* which were treated with a combination of nitrogen (0, 67, 134, and 202 kgN ha^{-1}), decreased hemicellulose, and increased the rate of lignin; the changes were small and approximately 2%. The location had a small but significant variation in cellulose (glucan), total hemicellulose (xylan + Arabian), and the holocellulose/lignin ratio (H:L) (Arundale et al. 2015). The variation in lignocellulose material may be due to the differences in soil fertility, precipitation, and temperature. Biomass variability was studied for 24 corn stover samples collected in 4 lowa countries, and a total of 216 samples with nine positions were analyzed: xylan (50.4–62.6%), glucan (47.1– 62.8%), and lignin (14.3–19.9%) showed similar results in all countries. Minor changes in biomass may be due to the biological degradation of bales (Ray et al. 2020).

9.6.2 With the Age of the Plant

The biochemical characteristics of plant biomass differ with age due to their capacity to uptake nutrients and adjustment to environmental stress conditions. The Three groups of *Miscanthus* were analyzed for biomass composition over three sequential years 2006, 2007, and 2008. The composition of cellulose (45–47%) and ADL (11.08–12.06%) increased, while hemicellulose decreased other groups of *M. sacchariflorus* and *M. sinensis* showed mixed results of increased and decreased values in cellulose, hemicellulose, and ADL composition. The results showed that cell wall biosynthesis in the three taxonomic groups might respond differentially to the climate, environmental conditions, and possible maturity stand of each year (Allison et al. 2011).

9.6.3 Climate Condition

The productivity of the crop depends on the precipitation pattern; the nutrient uptake and these parameters depend on the air temperature. The air temperature is influenced by climate change; in mild climates, the soil temperature is low, restricting the shoot growth. Increased soil temperature causes increased uptake of nutrients and water, contributing to an increase in root growth; the elevated temperature harms evaporation loss of water (Drebenstedt et al. 2023). For example, the effect of climate change on the variation in lignocellulosic chemical composition was observed for *Miscanthus* × *giganteus* cultivated in different climate regions in Russia from 2019 to 2021. Lignocellulosic characteristics variation studies on *Abies religiosa* with six altitudinal gradient levels that indirectly depend on climate, temperature, and relative humidity in Ejido El Conejo, Perote, and Veracruz, in Mexico. The average variation in chemical composition was approximately 54.81 ± 2.20% cellulose, 12.37 ± 1.33% hemicellulose, and 24.68 ± 1.16% insoluble lignin. The hemicellulose content of *Abies religiosa* increased with cooler temperatures along the altitudinal level, whereas lignin content was related to low temperature. Temperature and relative humidity decrease with altitude, and this environmental stress affect cell wall hemicellulose and lignin content (Musule et al. 2016). The physicochemical characteristics of soil, like soil moisture content, pH, organic matter, and total C and N, have a significant impact on plant biomass chemical characteristics.

9.6.4 Parts of Biomass Plants and Species

The distribution of nutrients in vegetative and reproductive growth is closely related to the internal structure of plant organs and the differentiation of tissue functions. It also reflects resource allocation patterns and plant growth strategies. *Ammopiptanthus mongolicus* shrub plant in China was studied for nutrient storage in leaf, stem, root, flower, and seed. The nutrient is concentrated in the seed > flower > leaf > root > stem order (Dong et al. 2023). The nutrient is more in reproductive organs for the maturation of seeds; usually, leaves store more nutrients than stems and roots for maintaining physical and ecological balance. As the stem is involved in transporting nutrients from roots to other parts of the plant, it has low nutrient storage than others. Work was conducted for NDF, ADL, cellulose, and hemicellulose determination for three taxonomic groups, with *M.* × *giganteus* having increased concentrations of NDF and cellulose and decreased concentrations of hemicellulose compared with *M. sacchariflorus* and *M. sinensis*. Variations among the three groups were observed as NDF (85–89%), cellulose (42–47%), hemicellulose (29–33.5%), and ADL (9–12%). The slight difference in biomass composition may be due to the parental plant's cell wall properties and the plants' reaction to environmental factors such as temperature and wind exposure to rainfall (Allison et al. 2011). A comparison was made for the chemical biomass composition of woody and herbaceous plants; the genotype of plants determines their phenotypic characteristics. Plant biomass genesis varies naturally and anthropogenically during plant growth, including photosynthesis, precipitation, evaporation, phase formation, local environmental conditions, and the mechanism of phase formation (Nanda et al. 2013).Variations in the lignocellulosic biomass composition of various plant species are provided in Table 9.2.

Table 9.2 Variation of lignocellulosic biomass composition for various plant species

S. no	Species	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
1.	Rice husk	–	27.4	–	Fermanelli et al. (2020)
	Peanut shell	–	18.8	–	
	Wheat straw	–	51.2	–	
2.	*M. giganteus*	47.09	29.43	11.76	Allison et al. (2011)
	M. sacchariflorus	42.94	32.50	10.15	
	M. sinensis	42.50	33.46	9.07	
3.	*Impereta cylindrica*	40	35–40	8–10	Singh et al. (2017)
	Eragrostis airoides	40–45	32–35	10–12	
	Typha angustifolia	35	28–30	10	
	Arundinella khasiana	35–40	15–20	10–15	
	Echinochloa stagnina	25	10–15	10–15	
4.	*Pinus banksiana* (pine wood)	38.8 ± 1.4	23.6 ± 0.8	20.4 ± 1.0	Nanda et al. (2013)
	Phleum pratense (timothy grass)	34.2 ± 1.2	30.1 ± 1.0	18.1 ± 0.7	
	Triticum aestivum (wheat straw)	39.1 ± 0.8	24.1 ± 0.6	16.3 ± 1.2	
5.	Brazilians sugarcane (RB867515)-Straw	42.12	35.93	12.04	Pereira et al. (2015)
	Brazilians sugarcane (RB867515)-Tops	35.02	37.27	8.95	
	Brazilians sugarcane (RB867515)-Bagasse	38.47	28.8	13.45	

9.7 Utilization of Agricultural Waste

9.7.1 Pyrolysis

Increasing agricultural waste's cellulose and hemicellulose content makes it suitable for pyrolysis because it increases the pyrolysis rate and rapidly decomposes into volatile products (e.g., bio-oil and NCG yield). The yield of gas, char, and bio-oil can be attained by varying the type of biomass, particle size, type of absorber/catalyst, and composition of mixtures. The volumetric concentration of CO, CH_4, and H_2 varies between 20% and 70% for wheat bran, rice husk, and nutshell (Fricler et al. 2023). Increasing lignin content reduces the pyrolysis rate as it retards the decomposition of volatile products and favors biochar yield (Onokwai et al. 2022).

9.7.2 Composting

Agricultural wastes are traditionally burned or landfilled after harvest to reprepare the land, which not only leads to environmental pollution but also causes nutrient loss in the soil. Instead of burning agricultural waste, massive amounts of agricultural waste can be converted into compost. The types of wastes involved in composting are rice straw, vegetables, sugarcane bagasse, straw, bran, and leaves. Compositing converts biodegradable organic matter-containing plants and animal waste, mediated by microbes under aerobic conditions, into humus soil, improving the soil quality for better crop growth and yield (Koul et al. 2022). Many factors, such as temperature, pH, moisture, oxygen, particle size, and the C/N ratio, affect the biodegradation rate of the composting process (Ho et al. 2022). The composting process comprises four stages: mesophilic, thermophilic, cooling, and maturation. During the mesophilic phase, the compost temperature was roughly 20–40 °C. Simple foods, such as sugars and proteins, are consumed by bacteria and fungi, leading to a second phase with an increased temperature of 45 °C. In the third stage, the compost pile's temperature decreased, and it reached the final stage of compost maturation (Sofia vizhimalar et al. 2022). The by-products of composting include H_2O, CO_2, NH_3, SO_4^{2-}, humic acid, and heat. Carbon and nitrogen formation decreased throughout the process. The pH initially decreased during the first stage and then increased at the end of the process (Chen et al. 2022). Equation (9.1) represents the reaction generated by new microbial cells (Ho et al. 2022).

$$\begin{aligned}&\text{Organic matter} + O_2 + \text{Nutrients} + \text{microbes}\\&\quad\rightarrow \text{New cells} + \text{Resistant organic matter} + CO_2 + H_2O + NH_3 + SO_4 + \text{heat}\end{aligned} \tag{9.1}$$

9.7.3 Methane Production

Biogas is an alternative renewable energy source to fossil fuels produced through the anaerobic digestion of vegetable waste, agricultural waste, fruit market waste, food waste, and municipal and industrial waste (Patel et al. 2022). Agricultural waste in biogas includes straw, plant corn, bamboo, and many more, of which corn stalks and maize have shown better yields than others (Sumardiono et al. 2022). Biogas is produced by microbes under anaerobic conditions through hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Gallego Fernández et al. 2022). Complex organic materials, such as cellulose, are converted into simple forms, especially glucose. Furthermore, glucose is modified into fatty acids and alcohols through acidification and is converted into methane by methanogenic bacteria (Sumardiono et al. 2022).

Lignin is a complex chemical structure that is an integral part of the cell wall and makes it the bacteria difficult to degrade cellulose; this effect reduces biogas yield.

The produced biogas consists of methane, carbon dioxide, and water vapor with small amounts of hydrogen sulfide and ammonia which, on compression of gas, tends to produce compressed biogas (CBG) with more than 90% of purified methane content, an alternative of compressed natural gas and a renewable transport fuel (Patel et al. 2022). The quantity and quality of obtained biogas depend on the nature of wastes given into the system of the digester like dry matter content, organic matter content, pH, and C/N ratio (Gallego Fernández et al. 2022).

9.7.4 Soil Reclamation

Soil degradation is the modification of soil's physical, chemical, and biological properties that aggravates the biological activity of the environment, food production, water quality, ecosystem, flooding, eutrophication, biodiversity, and carbon stock shrinkage. Soil degradation may be caused by geotechnical, physical, chemical, or biological factors (Kacprzak et al. 2022). The treatment and utilization of agricultural organic waste are essential for sustainable development worldwide. Agricultural organic waste reduces pollution and encourages recycling organic waste to improve soil fertility and structure, as organic wastes are rich in nitrogen, carbon, and phosphorus (Chen et al. 2021). Loamy sand soil after incorporation of agricultural waste after 7 months to a depth of 15 cm soil depth at 4 different rates (0, 2%, 4%, and 6% w/w) was analyzed for field capacity (FC), permanent wilting point (PWP) and infiltration rate (IR), etc. Increased soil organic matter improves soil hydraulic properties and porosity (Gülser and Candemir 2015).

9.8 Physical Treatment Methods

9.8.1 Pyrolysis

Pyrolysis is a thermal process that converts organic materials into carbonaceous materials, bio-oil liquids, and non-condensable gases in the absence or limited supply of oxygen at temperatures ranging from 300 to 700 °C (Bong et al. 2020). The pyrolysis process can be classified into conventional (slow), fast, and flash pyrolysis based on the heating rate and solid residence time. Conventional pyrolysis has a long residence time (hours to days) at low temperatures (300–700 °C), and this process allows the repolymerization of biomass, which results in the maximum solid yield. Fast pyrolysis involves high temperatures ($>$10–200 °C s^{-1}) with a short residence time (0.5–10 s) and bio-oil yields as high as 50–70% (w/w). Flash pyrolysis is characterized by a high heating rate of 10^3–10^4 °C s^{-1} and short residence time ($<$0.5 s), with a maximum yield of bio-oil as 75–80% (w/w) (Kan et al. 2016). The pyrolysis of biomass occurs in three stages: (1) initial evaporation of free moisture, (2) primary decomposition, and followed by (3) secondary reactions (oil cracking and repolymerization) (Wang et al. 2022).

9.8.2 Gasification

Gasification involves converting biomass materials into gaseous compounds, such as CH_4, H_2, and CO, in the presence of oxidizing agents, such as steam, air, O_2, and other gas mixtures. The gasification process generally yields approximately 85% syngas, 5% bio-oil, and 10% biochar (Vijayaraghavan 2019). Gasification with air produces syngas with low heating values of 4–7 MJ Nm^{-3}, while gasification with steam results in a high heating value of 10–14 MJ Nm^{-3} (Qian et al. 2015).

9.8.3 Hydrothermal Carbonization

HTC occurs at high temperatures like 160–800 °C in water, producing char frequently denoted as hydrochar. The reaction pressure must be increased (>1 atm) to maintain moisture in liquid form during the HTC process. The HTC process can be classified into two types based on the reaction temperature. Low-temperature HTC (<300 °C) and high-temperature HTC (300–800 °C). The HTC process is suitable for producing low-cost biochar when the feedstock has high moisture content. However, the characteristics of biochar obtained by the HTC process vary from those produced by the traditional pyrolysis process. The yield from slow pyrolysis and HTC is higher than gasification and fast pyrolysis (Vijayaraghavan 2019). Because the reaction of high-temperature HTC (above 300 °C) is above the stability of certain organic materials, the primary response during high-temperature HTC is hydrothermal gasification. The main products are gases, such as methane and hydrogen. The char yield of low-temperature biomass HTC varies from 30% to 60% depending on the feedstock properties, reaction pressure, and time (Qian et al. 2015).

9.9 Pyrolysis of Lignocellulosic Material into Biochar

Since the early period, people used fire for cooking, coal, and oil in fossil energy and electricity in the modern era, and the development of the human age has always concentrated on point. The use of plant biomass as an alternative source of fossil fuels for energy generation has recently increased (Canché-Escamilla et al. 2022). The annual production of lignocellulosic biomass accounts for 104.9 billion tons, mostly from rice husk and waste wood. The wastes for pyrolysis are sugarcane bagasse, corncob, nut shells, bamboo, rice and wheat straw, cornstalk, etc. Lignocellulosic biomass resources are burned directly, wasting resources and polluting the environment. Lignocellulosic biomass is a sustainable source of carbon that can be used as an energy source (Yu et al. 2022) (Fig. 9.3).

The thermochemical technologies for converting biomass into energy or chemicals includes combustion, pyrolysis, gasification, and high-pressure liquefaction (Kan et al. 2016). Slow pyrolysis is an efficient process for producing high-yield biochar. Biochar has attracted increasing interest and recognition as an efficient

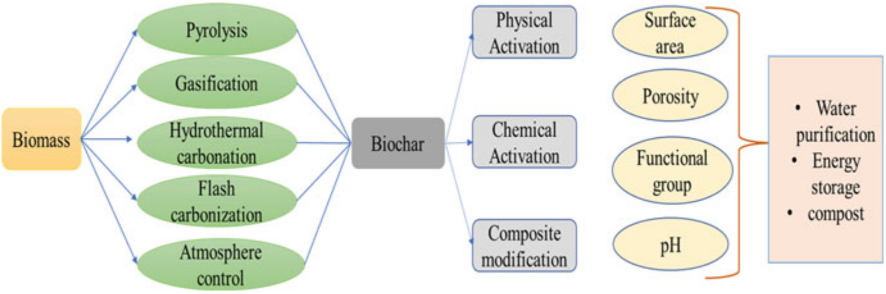

Fig. 9.3 Production and application of biochar

material for its wide applications, including soil amendment, climate change mitigation, environmental remediation, and functional material production for different industrial applications (Wang et al. 2022). The properties and yield of biochar depend on the characteristics of lignocellulosic biomass, particle size, heating rate, temperature, and residence time (Table 9.3). Different feedstocks produce biochars suitable for specific applications (Bong et al. 2020). Woody biomass contains about 51.2%, 21.0%, and 26.1% cellulose, hemicellulose, and lignin, respectively. The herbaceous biomass has been reported to be 32.1%, 18.6%, and 16.3%, respectively. Biomass with high lignin content tends to produce biochar with high fixed carbon, high specific surface area, and a more stable aromatic structure (Canché-Escamilla et al. 2022). Based on its physical and chemical characteristics, biochar can be used for contaminant removal from water and wastewater, catalysis, composting, fermentation detoxification, and electrochemical energy storage. The characteristics of biochar can be altered during post-treatment, such as activation and modification (Li et al. 2020).

9.10 Characterization Techniques of Biochar

9.10.1 Thermogravimetric Analysis (TG)

The behavior of the raw samples with different temperatures as a function of the heating time is monitored to find the maximum temperature for which residue turned into biochar (0.4 mm) was studied under an inert argon atmosphere in a standard thermogravimetric analyzer. A constant flow rate of 100 mL min^{-1} was applied. Each wood biomass sample (<10 mg) was heated in an alumina pan from room temperature to 1000 °C at 10 °C min^{-1}. Thermogravimetric tests were performed in an inert atmosphere (Ar) to evaluate the pyrolytic behavior of the biomass. They showed that the devolatilization process started before 100 °C, and the maximum weight loss is 230–360 °C. The interpretation of the weight loss of the samples between 230 °C, the end of moisture evaporation, and 360 °C indicated that 60–70%

Table 9.3 Percentage variation of biochar yield from different agricultural wastes

S. no	Type of biomass	Pyrolysis temperature	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Biochar yield (%)	References
1	Corn cob	600 °C	29.6	37.9	18.5	25.90	Wang et al. (2022)
2	Cornstalk		33.6	29.7	22.9	26.56	
3	Bamboo residue	500 °C	–	–	–	28	Khuenkaeo and Tippayawong (2020)
4	Coconut shell		–	–	–	26	
5	Corncobs		–	–	–	24	
6	Apa wood	700 °C	–	–	–	31.6	Titiladunayo et al. (2012)
7	Iroko wood			–		29.5	
8	Palm kernel shell					32.1	
9	Rice husk	500 °C		27.4		42	Fermanelli et al. (2020)
10	Peanut shell			18.8		29	
11	Wheat straw			51.2		28	
12	Hazelnut shells	700 °C	20.4	26.2	48.7	25.9	Martelo et al. (2022)
13	Nutshell	500 °C	35.70	18.70	30.20	60	Fricler et al. (2023)
14	Cashew nut	–	12.38	22.36	27.40	–	Stephen et al. (2023)
15	Cassava stem	–	38.90	15.32	22.71	–	
16	Almond fruit	400 °C	41.63	12.86	21.14	41–45	Suresh Kumar et al. (2022)

of the volatile matter was released, and the interval from 360 to 660 °C indicates the decomposition of carbon (Carrier et al. 2011).

The combustion of biomass takes place in two steps: the first is due to cellulose (280–400 °C) and hemicellulose (190–320 °C) and the second to lignin (320–420 °C). As lignin has an aromatic structure, it is expected to undergo combustion at a higher temperature than cellulose and hemicellulose, which are saturated compounds (Ghetti et al. 1996). Hemicellulose has a random amorphous structure with low strength, and its decomposition starts earlier. Cellulose is a very long polymer of glucose units without any branches, crystalline, and strong. Therefore, lignin is a polysaccharide composed of three heavily cross-linked benzene–propane structures. The maximum mass loss occurred between 200 and 600 °C due to increased evaluation of volatile cellulose, hemicellulose, and lignin compounds. Specific biomass has a low yield compared with the remaining biomass; this variation may be due to factors associated with the origin of each biomass residue, such as weather conditions, soil type, pH, and altitude, as well as the compositional variation and structural difference of the analyzed biomass waste (Yguatyara de Luna et al. 2019).

9.10.2 Brunauer-Emmett-Teller (BET) Analysis

The Brunauer-Emmett-Teller (BET) equation was initially developed to predict the monolayer coverage of nonporous materials from the measured multilayer physisorption of N_2 BET-based specific surface areas (BET SSA) and was subsequently developed for porous materials. In addition to N2, CO_2 is also used to characterize porous materials because (a) N_2 is kinetically unable to access pores (<0.5 nm) under measurement conditions, and (b) CO_2 facilitates monolayer adsorption and avoids the volume-filling effects commonly observed when using N_2 owing to the more significant quadrupole moment of CO_2 (Sigmund et al. 2017). During devolatilization, volatile matter escapes, resulting in the development of the internal surface area and porosity. The biochars were found to possess a lower BET surface area up to a higher pyrolysis temperature of 600 °C owing to the contraction of chars at post-softening and swelling temperatures. This resulted in narrowing or closing and confirmed the effect of pores (Vijayaraghavan 2019). During pyrolysis, some pores might have been blocked by the deposition of carbonaceous material after pyrolysis (Ahmad et al. 2007). Nitrogen absorption was negligible, indicating that the microporous structure was not fully developed. In a previous study, corncobs, cassava rhizomes, and cassava stems were analyzed for their BET; surface area during the pyrolysis heating process at 500–600 °C for 30 min was approximately 56.35, 18.38, and 200.46 $m^2\ g^{-1}$, respectively. A higher surface area facilitates increased ion exchange capacity. The pyrolysis temperature is an essential determinant of biochar's physical and chemical characteristics, as it governs the cleavage of the chemical bonds of cellulose, hemicellulose, and lignin (Wijitkosum 2023). The pre-treated rice husk and bagasse biochar had BET of 37.5 and 52.3 $m^2\ g^{-1}$, respectively, which are higher than that of Portland cement, resulting in increased pozzolan d cement (Asadi Zeidabadi et al. 2018).

9.10.3 Chemical Analysis

Proximate analysis determines the percentage of water, fixed carbon, volatile substance, and ash of the material (Table 9.4). The ultimate analysis is used to find the percentage of carbon, hydrogen, nitrogen, and oxygen in the material. The heating value of the material determines the usage of the material as fuel. The shell of residues is rich in cellulose, and the husk is enriched with lignin content. It was reported that increased lignin content tends to have high HHV than the residue with higher cellulose and hemicellulose.

An increase in temperature causes the weak bond to break and favors volatilization, increasing the carbon percentage (Rathod et al. 2023). During the thermal decomposition process, temperature increases with a decrease in the ratio of O/C and H/C. The biochar becomes more carbonaceous when the carbon percentage ranges between 53.6% and 68.6%. The O/C and H/C ratios of biochar are lesser than basic residues due to the loss of hydrogen and oxygen during thermal decomposition. Hydrogen bonding and van der Waals force bond the cellulose, hemicellulose, and lignin. The formation of new bonds liberates heat as it is an exothermic process. As per European Biochar Certificate (EBC), the biochar should have O/C and H/C values less than 0.4 and 0.7 for better fuel properties.

Samples showing a higher range of volatile matter are expected to produce better bio-oil yield. The bio-oil can be upgraded as chemical feedstock and fuel. If the samples are considered to have less fraction of nitrogen and sulfur, their contribution to air pollution is lesser (Park et al. 2012).The biochars with a higher carbon fraction are suitable for the torrefaction process as an alternative fuel source for boiler and heat treatment furnace systems. High moisture and ash content reduce the combustion efficiency and increase the burning time. Hence, it requires specific pre-treatment before its fuel application. The pre-treatment includes cutting the raw sample to minimize moisture and washing the biochar to reduce the ash content (Table 9.5).

9.10.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used for structural analysis and characterization of the functional groups on the carbon surface produced by vibration. For FTIR analysis, an FTIR spectrophotometer was operated in the attenuated total reflection (ATR) mode with a wavelength range of 500–4000 cm^{-1}. The lignocellulosic materials showed the band between 690 and 515 cm^{-1} was attributed to the C–Br strectching of halo compound (Karthikeyan et al. 2019). C–H bending occurs in the 750–850 cm^{-1} as alkene groups (Kaur et al. 2022). The C=C bending bond occurred between 850 and 980 cm^{-1} (Karthikeyan et al. 2019). The band at approximately 1100–1000 cm^{-1} corresponds to C–O, C=C, and –C–C–O stretching in cellulose, hemicellulose, and lignin (Kaur et al. 2022). The band at 1210–1100 cm^{-1} is ascribed to C–O stretching in the ester groups (Kaur and Sharma 2019). The crew of alkane stretching encountered at 1475–1350 cm^{-1} (Chandran et al. 2020). The band at 1500–1400 cm^{-1} is

Table 9.4 Ultimate, proximate analysis and heating value for various agricultural residues

S. no.	Feedstock	Elemental composition %				W %	FC %	VS %	A %	LHV (MJ kg^{-1})	HHV (MJ kg^{-1})	References
		C	H	N	O							
1	*Amaranthus retroflexus*	37.6	5.4	1.3	44.7	83.8	47.74	20.38	31.88	–	14.6	Karaeva et al. (2022)
2	Maize stalk	49.22	6.05	0.80	43.82	5.50	12.71	71.69	10.10	17.50	–	
3	Pinewood	50.9	6.20	0.10	42.8	7.2	8.9	83.6	0.3	–	–	Ge et al. (2023)
4	Straw	42.9	5.86	0.48	50.8	0.2	16.2	74.4	6.2	–	–	
5	Garlic stem	42.29	6.03	3.84	47.84	5.81	2.21	83.18	8.80		18.36	Park et al. (2012)
6	Pepper stem	46.23	5.60	1.75	46.42	2.82	23.30	68.60	5.82		19.39	
7	Groundnut shell	50.9	5.15	0.58	42.1	9.5	11.78	74.6	4.12	13.35	15.68	Rathod et al. (2023)
8	Cashew nut	54.51	0.87	1.26	43.24	7.71	85.26	5.14	1.89	–	31	Stephen et al. (2023)
9	Corn cob	50.33	1.52	1.09	46.97	13.4	67.94	9.26	9.40	–	26.42	
10	Almond fruit	50.72	4.98	1.86	42.44	12.32	15.16	61.14	11.38	–	18.31	Suresh Kumar et al. (2022)
11	Cull potatoes	39	6.31	1.10	49.1	11.6	17.3	78.3	4.40	–	–	Vilakazi et al. (2023)
12	Amarnath inflorescence waste	41.83	6.81	4.71	37.89	7.42	9.17	74.65	8.76		17.87	Karaeva et al. (2023)
13	Mustard husk	44.47	6.03	0.54	48.09	6.40	20.62	69.30	3.68	–	–	Kakku et al. (2023)
14	Cotton stalk	44.94	7.32	0.69	46.85	4.50	19.67	71.10	4.73	–	–	
15	Wheat straw	43.80	5.48	0.62	38.69	6.53	18.19	70.50	4.78	–	17.52	Muzyka et al. (2023)

Table 9.5 Ultimate, proximate analysis and heating value for various agricultural biochar 10.4 Fourier Transform Infrared Spectroscopy (FTIR)

S. no.	Biochar	Temperature	Elemental composition %				W %	FC %	VS %	A %	LHV (MJ kg^{-1})	HHV (MJ kg^{-1})	References
			C	H	N	O							
1	Groundnut shell	500 °C	89.03	2.19	0.21	4.48	2.13		13.92	24.71	23.55	25.18	Rathod et al. (2023)
2	Cull potatoes	650 °C	71.5	1.74	1.45	9.74	6.08	70.08	14.45	15.48	–		Vilakazi et al. (2023)
3	Corncob		–				18.67	26.03	48.97	6.33	–	22.05	Khawkomol et al. (2021)
4	Coconut shell						2.96	53.99	38.63	4.42	–	23.60	
5	Amarnath inflorescence waste	500 °C	56.56	3.09	4.12	15.75	4.4	53.77	21.34	20.49	–	20.92	Karaeva et al. (2023)
6	Bamboo chopsticks	500 °C	63.47	2.83	0.65	29.11		52.73	35.99	3.80	–	–	Wijitkosum (2023)
7	Cotton stalk	500 °C	63.10	2.07	1.80	32.65	5.30	36.85	38.62	19.23	–	–	Kakku et al. (2023)
8	Mustard husk	500 °C	61.80	2.65	1.49	33.77	6.12	15.47	59.47	18.67			
9	Wheat straw	500 °C	65.50	3.51	1.29	11.03	3.63	57.85	23.69	14.83		25.07	Muzyka et al. (2023)
10	Date palm leaf	600 °C	64.13	2.20	1.95	4.67	–	65.31	11.45	23.24			Schmidt et al. (2023)
11	Pistachio shell	600 °C	88.55	1.74	0.32	11.20	–	89.69	8.97	1.34	–	–	

attributed to the O–H bending carboxylic acid groups. The nitro compound absorptions cause the bar at about 1560–1500 cm^{-1}, while C=O stretching carboxylic acid occurs around 1900–1850 cm^{-1} (Kiran and Prasad 2019). The bar at 2000–1900 cm^{-1} could be attributed to C=C=C stretching in the allene groups. The appearance of rounds between 2140 and 2100 cm^{-1} could be assigned to C≡C stretching in the alkyne group, and the subsequent bands at 2145–2120 cm^{-1} correspond to N=C=N stretching in carbodiimide. The shoulder at 2350–2300 cm^{-1} could be assigned to O=C=O stretching in the carbon dioxide group and the intense band across 2600–2550 cm^{-1} to S–H as thiol groups. The C–H stretching in aldehyde occurs around 2830–2695 cm^{-1} (Jayakishan et al. 2019), and C–H is trying in alkene in 3100–3000 cm^{-1} (Manikandan and Subramanian 2013). The N–H stretching of primary aliphatic amine peaks between 3500 and 3300 cm^{-1}, while O–H stretching alcohol groups were present in around 4000–3500 cm^{-1} (Kaur and Sharma 2019). The surface chemistry study of the FTIR of carbon showed similar functional groups with dominant carboxylic, ester, phenol, alkane, and amine groups. The formation of functional groups occurred because of the decomposition of cellulose, hemicellulose, and lignin at high pyrolysis temperatures (Chia et al. 2012).

9.10.5 Scanning Electron Microscopy (SEM)

SEM was used to investigate the surface structures of the biochar and activated carbon. SEM has been used to study the ultimate composition and morphology of carbon, such as iron-impregnated biochar before and after sorption, MPB, BPB, magnetic biochar (natural hematite, pinewood), magnetic and nonmagnetic energy cane, ZVI biochar, clay biochar carbon composite, magnetic oak wood, and bark biochar, MgEC, biochar/MgAl-LDH (composites), biochar/γ-Fe_2O_3 (composite), biochar/AlOOH nanocomposite, sewage sludge biochar, DAWC and DWSBC, MgO-biochar nanocomposite, chicken manure and green waste biochar, cottonseed hull biochar, DSTC for the removal of metals/non-metals, micro-and macronutrients, and PAHs from soil and aqueous removal (Amin et al. 2016). The biomass contained muscular bulky xylem tissues. The biomass begins to lose its bound fibrous structure, cracks, and fissures upon activation. The samples showed significant differences in surface topography, such as spongy, smooth, and rough surfaces: honeycomb and graphite structures with a close and deep cavities-like appearance. The developed pores are micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Upon activation above 600 °C for a specific residence time, the temperature causes the volatile substance to escape, resulting in modified pores and a modified BET surface area (Vijayaraghavan 2019).

The development of the pore texture and surface morphology of the activated char was investigated by scanning electron microscopy (SEM). Carbon was coated with gold to avoid electrical charge deposition and improve the resolution. Sputter Coating Cressington 108 model did the gold coating at 10 nm thick for 40 s. Carbon was analyzed using a QUANTA 200F instrument at an accelerating voltage of 30 kV. Porosimetric analysis was performed using a porosimeter. N_2 gas was used as the adsorbate, and the system was operated at −196 °C. Before the experiment, the sample was outgassed at 160 °C for 12 h to remove moisture and other impurities. The total pore volume V_T was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure of $P/P^0 = 0.99$ (Vargas et al. 2011).

9.10.6 X-Ray Diffraction Measurements

X-ray diffraction examines the crystalline material structure and size. Powder X-ray diffraction spectroscopy (XRD) analyses were carried out with D8 Advance (Bruker). The Cu-Kα X-ray source had a wavelength of 1.54°A. The voltage was 40 kV, while the current was 15 mA. The samples were then gently mounted on an X-ray diffraction (XRD) machine. The test was carried out in continuous scanning mode with a step size of 0.002 and a 5°/min speed. The diffraction data were collected over a 2-theta range of 4–90°. The phases in the diffraction pattern were identified by analyzing the data using the X'Pert High Score Plus software (Yaashikaa et al. 2020). The minerals present in activated carbon may act as ion exchange sites with the adsorbate for adsorption. The high-intensity peak at $2\theta = \sim 23°$ and low-intensity peak at $2\theta = 43°$ indicate the presence of the crystalline structure of the activated carbon (Kaur et al. 2022). A study on corn stover showed that charcoal decomposes hemicellulose and cellulose microcrystalline graphite with increasing temperature with a degree of crystallinity, which leads to a more stable conversion of carbon compounds. Metal oxides precipitate mineral salt and then convert to acetals and finally to carbonates at the pyrolysis temperature; with increasing temperature, the content of $CaCO_3$ increases (Zheng et al. 2016). Pyrolysis of natural hematite and pinewood biomass showed the diffraction of biochar at 30.2°, 35.5°, 43.2°, 57.3°, and 62.9°, assigned to $\gamma = Fe_2O_3$ (Wang et al. 2015). The XRD image of pitch pine biochar showed a peak at 23° owing to the formation and successive ordering of aromatic carbon, which began to decompose the nanocomposite during the charring process (Kim et al. 2012).

9.11 Influence of Lignocellulosic Composition on Pore Formation

The chemical structures and thermal stabilities of cellulose, hemicellulose, and lignin polymers in plant biomasses differ. Their proportions varied widely between biomass types and parts. Cellulose and hemicellulose have simple monomers that decompose at low temperatures (450 °C), are primarily light molecular weight compounds, and are released as pyrolytic vapors. In contrast, lignin amorphous and hydrophobic polymers contain numerous functional groups with aromatic carbon sub-structures that decompose over a wide range of temperatures and contribute more biochar, leaving condensed aromatic carbons with reduced functional groups. Char yielded 23.5% hemicellulose, 19% cellulose, and 45% lignin. Specific surface area and pore development occur for biomass materials with a vascular structure, such as bagasse and wood stem (longitudinal pores), while wood bark lacks a vascular structure (Lee et al. 2013).

A study compared pore development in palm shell and coconut shell-activated carbons under identical experimental conditions. Palm shell contains cellulose, holocellulose, and lignin in 29.7%, 47.7%, and 53. 4%, respectively, while coconut shell has 19.8% cellulose, 68.7% holocellulose, and 30.1% lignin. The BET surface areas of the palm and coconut shells were approximately 260 and 163 $m^2 g^{-1}$. Within the range of burn-off studied, the micropore and mesopore volumes were compared between palm shell and coconut-activated carbon at any burn-off. The nature of the starting material largely determines the pore structure and pore size distribution of activated carbon. The lignocellulosic contents were determined by the Technical Association of Pulp and Paper Industry (TAPPI) (Daud and Ali 2004).

An investigation was carried out for the contribution of hemicelluloses, cellulose, and lignin to the carbon mass yield and the textural properties of activated carbons produced from lignocellulosic precursors by phosphoric acid activation. The raw materials of the four lignocellulosic precursors (olive pomace, miscanthus, tomato plants, and poplar wood) were treated thermally with or without an activating agent. The yield of lignocellulosic precursors was similar and had a low porous surface area. This may be due to differences in the morphology and arrangement of the three compounds within the plant's raw material. The concentrations of cellulose, hemicellulose, and lignin varied from 23.05% (olive) to 38.65% (*Miscanthus*), 33.20% (olive) to 40.90% (poplar wood), and 20.55% (tomato plant) to 43.75% (olive). The maximum BET surface area attained for poplar wood was 483 $m^2 g^{-1}$, followed by olive pomace (144 $m^2 g^{-1}$) and *Miscanthus* (68 $m^2 g^{-1}$) to a minimum surface area of 40 $m^2 g^{-1}$. The yields of lignocellulosic precursors were similar and had a low porous surface area. This may be due to differences in the morphology and arrangement of the three compounds within the plant's raw material. The yield with the activating agent was similar to and higher than that obtained without the activating agent. The material with lignin is microporous and has a low external specific surface area, whereas cellulose is mesoporous and has a high specific surface area (Boundzanga et al. 2022). The study was done to determine the relationship between different material compositions and the structure of activated carbon; a series of different mass ratios of cellulose and lignin were prepared as pure cellulose (AC-1), 3.5:1 (AC-2), 3.5:3.5 (AC-3), and 3.5:5 (AC-4). The materials were activated with $ZnCl_2$ via microwave heating. The structural difference was observed among different ratios of AC; as the lignin content increases, the BET surface area decreases (1077.54 $m^2 g^{-1}$ for AC-1 to 558.48 $m^2 g^{-1}$ for AC-5), whereas the total pore volume, mesopore volume, and average pore width initially increased and then decreased. This is because of the biomass's cellulose (polysaccharide and hydrogen bonds) and lignin (polyphenolic macromolecule) content variations (Xue et al. 2018).

9.12 Application of Biochar (Fig. 9.4)

9.12.1 Soil Application

Soil characteristics determine crop production, biota, and human life in an ecosystem for a better environment. Pollutant concentration, microbial activity, climatic conditions, and land use modify soil quality in various ways. Several techniques, such as applying additives (e.g., biochar), have improved soil properties. Biochar is a carbon-rich solid product of pyrolysis at 250 °C with a high carbon content and a large surface area required for soil amendment (Kamali et al. 2022).

Biochar produced at 400, 450, 500, and 550 °C was mixed with soil at ratios of 1:2, 1:4, and 1:5 to cultivate *Allium sativum* L. garlic plants. Investigated for heavy metal accumulation in the plant, the biochar prepared at 450 °C with a soil ratio of 1:4 showed a maximum yield of garlic plant and minimum uptake of Zn and Cu metals. Increasing the ratio of biochar in the soil increased the nutrient supply and maximum garlic yield. This is suitable up to an optimum ratio of biochar (1:4 or 1:5); this characteristic is influenced by the soil properties, temperature, and feedstock for char production (Song et al. 2014). A study was conducted on application of sewage sludge biochar with 5% and 10% to the paddy soil to reduce the bioavailability of potentially toxic elements (PTEs). Thus, the modified soil there by reduces the bioaccumulation of carcinogenic metals in paddy field, and reduces the cancer risk by 66% (Khan et al. 2014). *Eucalyptus globulus*, corn cob, and *Lantana camara* biochars were applied to the soil with 6, 12, and 18 t ha^{-1} at a depth of 0–15 cm at 3 levels for each sample, with 3 replications in Southern Ethiopia. Soil plots were analyzed for acidity and physicochemical properties at 0–30 cm depths for bulk density, total porosity, pH, soil organic carbon, total nitrogen, available phosphorus, potassium, and exchangeable acidity before and after the addition of biochar.

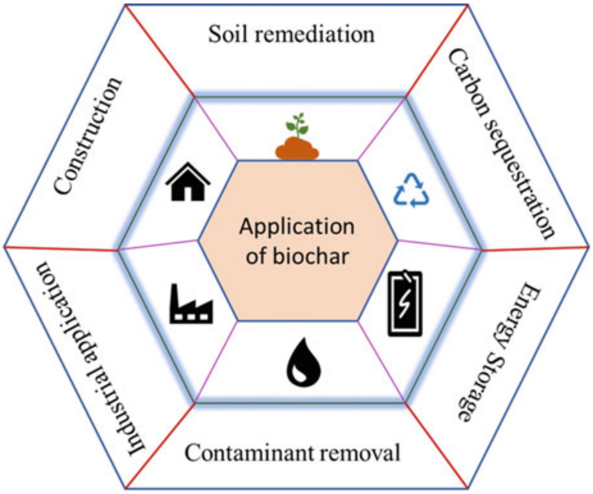

Fig. 9.4 Application of biochar

Among all applied biochar treatments, *Lantana camara,* with 18 t ha^{-1}, had the highest modified soil properties, especially because it reduces soil acidity with biochar application to the soil (Berihun et al. 2017).

9.12.2 Contaminant Removal from Water and Wastewater

Heavy metals, which are major contaminants in the environment, degrade the surrounding in several ways. When inefficiently treated wastewater containing heavy metals is used for irrigation, crops can take up heavy metals, and the organic dyes which are frequently utilized in paint, textiles, leather, and culinary applications. Only 5% of the dyes are effectively used in the dyeing process, and the remaining dyes are discharged into the environment (Ye et al. 2023). An investigation was conducted to study the adsorption of Zn (II) using agricultural waste (coffee pulp, banana pseudo-stem, and corncob). Coffee pulp showed a maximum removal of 63.58% of Zn (II), and the material was studied for optimum pH, kinetics, adsorption isotherm, and point of zero charges (Aguilar et al. 2020). Pistachio wood waste was activated in one stage with NH_4NO_3 at different impregnation ratios (0–10%) at different temperatures (400–900 °C) for maximum mercury adsorption. The best result was obtained at an activation temperature of 800 °C for a pyrolysis time of 2 h with an impregnation ratio (NH_4NO_3/precursor; wt%) of 5%. PWAC had a larger BET surface area and total pore volume (1448 m^2 g^{-1} and 0.901 cm^3 g^{-1}) at 800 °C. PWAC has a healthy, regular-shaped, amorphous porous structure. This is due to NH_4NO_3 melting and diffusion into lignocellulose and microcracks due to higher stress at higher temperatures (210–220 °C), causing cellulose to degrade. Further increases in the temperatures of 260 and 300 °C made the NH_4NO_3 explode, a critical step in opening the pore. The XRD analysis showed that crystallinity and pH_{zpc} (9.6) resulted in better adsorption of Hg (II). A pH ranging from 6 to 10 Hg $(OH)_2$ is the dominant favored H-Cπ bonding. At pH values lower than 4, AC has a protonated functional group, and Hg^{2+} inhibits mercury removal. At pH 4–6, Hg was removed as Hg $(OH)_2$. A kinetic study was conducted to evaluate the system design. Interparticle diffusion is more common in PWAC due to parallel pores. The maximum Hg (II) adsorption capacity was 201 mg g^{-1} (Sajjadi et al. 2018).

The banana peel was activated by physical (carbonation under microwave irradiation) and chemical (mixture of KOH/NaOH, KOH, and NaOH) processes under microwave irradiation. Volatilization during the carbonation stage is followed by forming new pores and widening existing pores by chemical activation. The carbon yield of KOH activated carbon (22%) is less compared to NaOH (25%), as KOH (low ionization) is more alkaline than NaOH. Upon chemical activation with KOH/NaOH, the increased OH– ions react with oxygenated –COOH–, C–O functional groups liberate oxygen compounds such as CO2 and CO; hence, oxygen content decreases. Char carbon is a good microwave absorber, which results in dipole rotation and increased decomposition. BET increased from 320 to 1130 m^2 g^{-1}, and pore volume ranged from 0.2 to 0.80 cm^3 g^{-1} (for combined

KOH and NaOH) and removed 90% of malachite green dye with 22.5 mg g^{-1} adsorption capacity (Liew et al. 2018). A study on bamboo powder was pyrolyzed and activated using NaOH at 300 °C, and the activated carbon was then ball-milled to increase its surface area. The activated carbon was analyzed for the adsorption of Pb (II) and methylene blue (MB, 419.11 mg g^{-1}) at 308 K. Based on optimum studies on different working parameters, such as concentration, temperature, pH value, and ionic strength, it was found that the adsorption process followed pseudo-second-order kinetics and the Langmuir model ($R^2 > 0.9924$); adsorption was thermodynamically endothermic and occurred spontaneously. Hence, alkali-modified bamboo biochar can efficiently remove heavy metals and cationic pollutants from wastewater (Ye et al. 2023).

Investigation for the removal of sulfamethyldiazine (SM), sulfamethazine (SM2), sulfathiazole (ST), and sulfamethoxazole (SMX) on a spent mushroom substrate (SMS) was carried out for the contact time, initial concentration (0.5–10 mg L^{-1}), and pH (1–11), and the concentration of antibiotics; the concentrations were analyzed by HPLC. Kinetic studies were performed using pseudo-first-order, pseudo-second-order, and intra-particle models. The adsorption isotherms were modeled using Langmuir and Freundlich models. The adsorption fitted-well with the Langmuir isotherm and with maximum adsorption capacities of 2.1, 1.8, 2.3, and 2.2 mg g^{-1} at 288 K for SM, SM2, ST, and SMX, respectively. Therefore, spent mushroom substrate could be an alternative material but too expensive adsorbents for removing trace sulfas (Zhou et al. 2016).

9.12.3 Electrode Material

Carbon materials have been continuously developed for use in supercapacitors in recent years. Supercapacitors can be classified as pseudo-capacitors (PCs) and electrochemical double-layer capacitors (EDLCs). Through electrostatic forces between the solid electrolytes, these electrodes store charges on the electrode to realize energy storage. Pseudo-capacitors work via a reversible oxidation-reduction mechanism (Jiang et al. 2013). In EDLCs, two layers of ions with opposite polarities are formed when a voltage is applied across the contact boundary. The charging and discharging follows electric double layer mechanism in pseudo-capacitive materials such as metal oxides, transition metal oxides, conducting polymers and carbon-based materials (Zhang et al. 2014). Owing to the declination of nonrenewable energy, EDLCs act as excellent energy storage devices because of their high specific capacitance, high power density, better cycle efficiency, and long cycling stability (Qiu et al. 2018). Supercapacitors have applications in electrical automobiles, electrical and uninterruptible power supplies, and power tools. Carbon materials are suitable for electrodes because of their excellent electrical conductivity, electrochemical stability, and natural abundance (Gupta et al. 2015). Biochar with different physical and chemical stabilities and functional groups on its surface can be prepared by modifying its preparation conditions. Activated carbon is mainstream, whereas nano-carbons enter the market as costs decrease (Li et al. 2021). The higher the surface area of the carbon, the greater its specific capacitance; however, in practice, some carbons with a smaller surface area have more specific capacitance as the situation becomes more complicated. The capacitance depends on the type of carbon, methods of preparation, accessibility of pores to electrolytes, and surface reactions that contribute to the charge and discharge processes (Jiang et al. 2013).

Electrodes prepared from millet straw-activated carbon (MAC) and anthracite coal-activated carbon (AAC) were made by thermal modification with KOH: C with a ratio of (5:1) for supercapacitor (SC). In the EIS test, the ESR (0.28 Ω) of the AAC electrode was 6.5 times more efficient than that of the MAC electrode (0.043 Ω). In a GCD test, the specific capacitance of MAC is more than AAC. The activated biochar had a specific capacitance of 144 F g^{-1}, while AAC had 85.2 F g^{-1} at the current density of 0.2 A g^{-1}. In a cyclic performance study, the MAC was 125%, greater than the AAC of 114% at a current density of 0.5 A g^{-1}. MAC performance shows that an excellent supercapacitor can be obtained by activating cheaper millet straw biochar as an electrode (Ding et al. 2020).

The supercapacitor performance was analyzed using carbon material from corn straw biochar. The corn straw was pyrolyzed at 450 °C in a homemade fluidized bed reactor followed by activation with different ratios of KOH (KOH: biochar-1, 2, 3, 4) at 800 °C under an inert atmosphere for 1 h, and the biochar was named BBC-1, BBC-2, BBC-3, and BBC-4. SEM, The carbon material was characterized using TEM, EDS, and XPS. A semiconductor resistivity tester measured XRD, Raman spectra, and electronic conductivity. Pores of the carbon material were found by N_2 adsorption data using BET; BBC had polypores and a high specific surface area. At the same time, BBC-4 had shown excellent capacitance of up to 327 F g^{-1} in the presence of both acid and neutral electrolytes with high-rate performance and high work voltage of up to 1.6 V. The stability of biochar extends to 120,000 cycles with an energy density of 20.2 Wh kg^{-1} (Qiu et al. 2018). The capacitance of biochar from maple wood was studied by pyrolysis at 750 °C for 2 h in an N_2 atmosphere and as a supercapacitor electrode material. The electrode material was fabricated as mini-chunk, thin film, and large-disk-chunk electrodes. The capacitive of the electrode was tested using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The electrochemical behavior of the mini-chunks and thin film electrodes was similar and had a specific capacitance of 32 F g^{-1} with potential stability cycles of 26,000. Hence, mini-chunk electrodes can be used as an mF-scale power source for electronic applications. They are efficient supercapacitors because of their high potential, low cost, and environmental friendliness (Zhang et al. 2014).

9.13 Summary

Agricultural wastes are of great interest for research as they are rich in nutrients and can produce by-products with rich nutrient content. The biochemical composition of the wastes varies with various parameters of the ecosystem, and the effective utilization of waste reduces pollution and solves waste disposal problems. The wastes can be biologically degraded to produce biogas, compost, soil reclamation, etc. The biochar can be modified physically, chemically, or biologically for suitable application in water purification as catalysts, construction materials, etc. Therefore, proper maintenance of rules, regulations, and various acts upon producers, distributors, and users have to be monitored by accountable authorities to limit agricultural pollution. Moreover, introducing new regulations/acts/policies/schemes in these lines would encourage the conversion of agricultural waste into value-added products.

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Agricultural Waste-Based Biochar for Soil Carbon Sequestration and Emission Reduction: Preparation, Evaluation, Application, and Mechanism

10

Longfei Liu, Shengsen Wang, Chenhao Zhao, and Xiaozhi Wang

Abstract

To cope with global warming caused by the disruption of CO_2 balance, carbon capture and sequestration are considered to be one of the most effective solutions at present. It is of great significance for the conversion of agricultural waste generated globally every year into biochar with strong affinity for CO_2 to achieve "carbon sequestration and emission reduction." In this chapter, the properties of agricultural waste-based biochar (AWB) related to carbon fixation and sequestration were first summarized in terms of feedstock type and pyrolysis temperature. Some commonly used methods of biochar modification were also described. Greenhouse gas (mainly CO_2) balance model and energy balance model are used to evaluate the carbon fixation and emission reduction capability of AWB during its life cycle. Then the effects of different AWB used for carbon sequestration were reviewed and discussed in detail. In addition, the carbon sequestration and emission reduction mechanisms of AWB in soil were analyzed and summarized. The specific surface area, micropore volume, hydrophobicity, and alkaline groups of AWB become the key to the carbon sequestration capacity of AWB. Soil pH, moisture, and microbial abundance were also important factors affecting the carbon sequestration capacity of AWB. Finally, the current situation and problems of AWB for carbon sequestration and emission reduction were presented. AWB will be a promising solution to address global climate change.

Keywords

Agricultural waste · Biochar · Soil · Carbon capture and storage · Influencing factors · Mechanisms

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10.1 Introduction

Agricultural wastes are referred to by-products generated in agriculture and the processes related to agricultural production and processing. According to the source of biomass wastes, they can be divided into primary biomass waste, secondary biomass waste, and treated (processed) biomass waste. It is reported that about 998 million tons of agricultural wastes are produced every year (Duque-Acevedo et al. 2020). Among them, plant residues such as straw of various crops, fruit peel, waste wood, waste mushroom residue, etc. represent the main agricultural wastes. The utilization of agricultural wastes is relatively extensive (Fig. 10.1), and the most common ways of resource utilization are as follows. First, straw-based agricultural waste is directly returned to the field, which does not result in CO_2 emissions nor CO_2 emission reduction. However, straw return to the field may increase CH_4 emission as well as intensify the occurrence of pests and diseases, and the soluble organic matter produced by straw decomposition may cause water pollution and other problems (Jin et al. 2020). In the second route, the biomass are composted and then returned to soil as a soil amendment. Although the composted biomass can increase the soil carbon pool slightly, the production and application of compost will bring a large amount of greenhouse gas (CO_2, CH_4, N_2O) emissions (Zhu-Barker et al. 2017). Third, combustion of biomasses is another common techniques to treat the waste biomass, which are often used for energy generation (Wang et al. 2022).

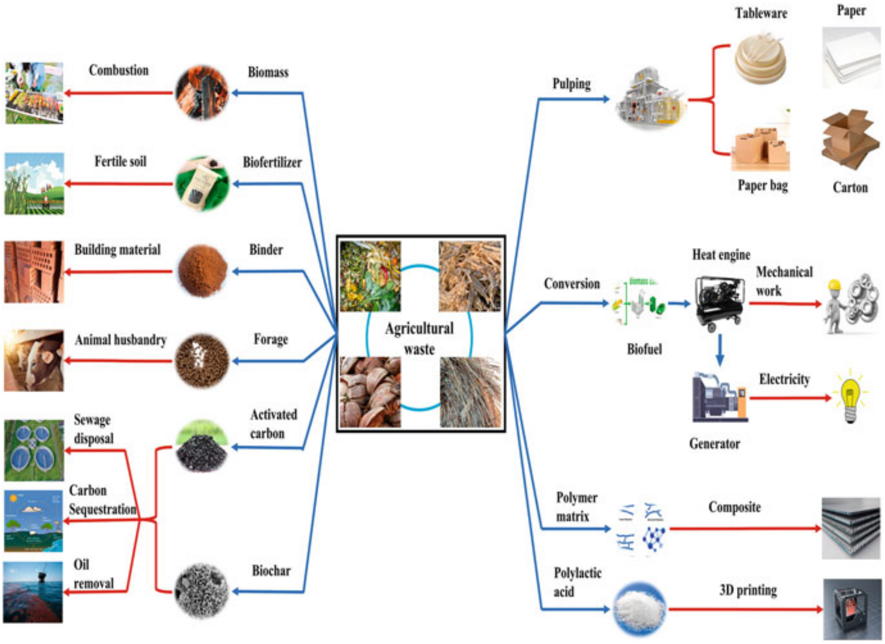

Fig. 10.1 Conversion and application of agricultural wastes

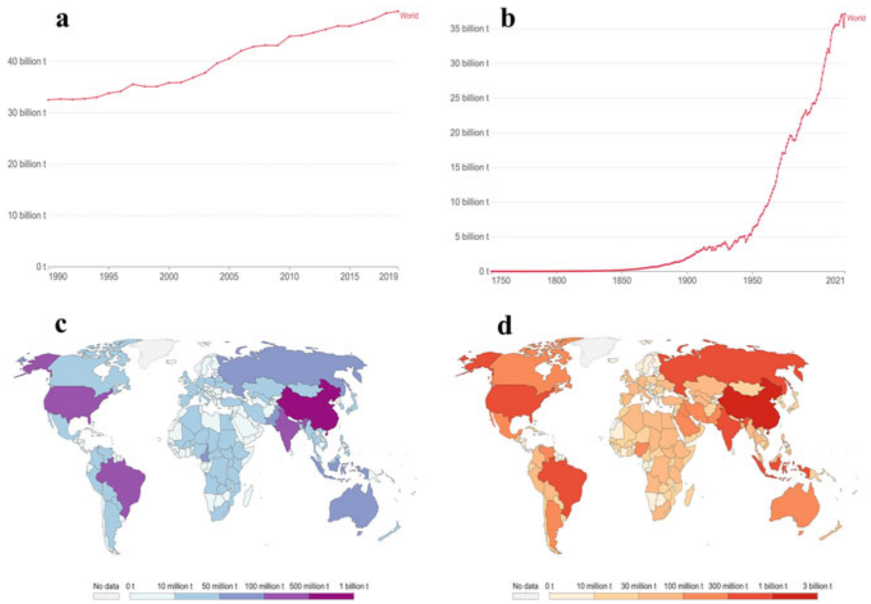

Fig. 10.2 (**a**) Total greenhouse gas emissions. (**b**) Annual CO_2 emissions (**c**) N_2O emissions in 2019, and (**d**) CH_4 emissions in 2019. N_2O and CH_4 emissions are measured in tons of CO_2-equivalents. (Data source: Our World in Data based on Climate Analysis Indicators Tool)

However, the cost of direct combustion for power generation has been high due to low energy density and high costs associated with collection, transportation, and costly operation equipment. Another problem that cannot be ignored is that biomass waste from different sources may have various potentially harmful substances, such as pathogenic bacteria, insect eggs, pesticide residues, pathogenic bacteria, antibiotics, and heavy metals. Therefore, the utilization of agricultural waste in an efficient and safe way has become an important research topic for sustainable development.

With the development of industry, global warming has become an important environmental issue to be faced by humans. Since 1950, global greenhouse gas emissions have increased dramatically, resulting in a considerable concentration in atmosphere (Fig. 10.2a). Compared to N_2O (Fig. 10.2c) and CH_4 (Fig. 10.2d), the annual emissions of CO_2 (Fig. 10.2b) are even more rapidly increased to over 34 billion tons annually in 2021 (Fig. 10.2b). According to the estimation of Intergovernmental Panel on Climate Change (IPCC), the CO_2 concentration (550 μmol mol^{-1}) in the atmosphere has doubled compared with that before the industrial revolution (380 μmol mol^{-1}). The concentration of CO_2 in the atmosphere may rise to 700 μmol mol^{-1} by the end of this century. Although CO_2 emission has slowed down in recent years due to people's concerns and related measures, the atmospheric CO_2 concentration still does not reach the peak (Schmidt et al. 2014). To combat CO_2 rise, many countries have proposed corresponding management measures. At the Paris Agreement in 2015, the participating countries agreed to limit the global average temperature rise to 2 °C or even lower than pre-industrialization levels. In 2020, the Chinese government announced that it would strive to reach the peak of CO_2 emissions by 2030 and strives to achieve the carbon neutrality target by 2060. Carbon capture and sequestration are considered to be the most economical way to reduce greenhouse gas levels on a large scale in a short period of time. It is also considered to be the most economical method to achieve effective CO_2 emission reduction. The World Development Bank predicts that global CO_2 emissions can be reduced to 1428 Mt by 2050 through the use of carbon capture and carbon storage technologies.

Soil is one of the important sources of global greenhouse gas emissions based on frequent agricultural cultivation, active carbon and nitrogen cycles in the soil, plant and soil animal life activities, etc. In particular, inappropriate farming practices, such as excessive application of nitrogen fertilizers, would lead to the emission of large amounts of greenhouse gases from soils. In addition, as the core of terrestrial ecosystems, soil is the largest terrestrial carbon pool. The carbon stored in soil carbon pool is about three times that in the atmosphere. Therefore, the rational management of soil carbon pool is of great importance to global climate change. At present, due to human intervention, the carbon consumption rate balance in the soil has been broken. Thus, the soil carbon pool is far from saturated. This provides a very good potential and opportunity for soil carbon sequestration. Therefore, using soil as a carbon sink is an important way to reduce carbon emissions and mitigate global climate change.

Some common materials, such as mesoporous carbon, zeolite, activated carbon, etc., have been used to study the adsorption and fixation of CO_2 and CH_4 in the past few years. These adsorbents can show good performance in carbon capture and carbon sequestration. But some shortcomings are also shown in the actual operation process, such as high cost, difficult regeneration, and competitive adsorption. Biochar, as a carbon-based material with a rich porous structure, has been widely used for the removal of organic pollutants and heavy metals from water and soil, soil quality improvement, and energy production because of its low cost, rich functional groups, large surface area, and microporous volume. The application of biochar to soil can return and preserve the carbon fixed by plant photosynthesis in soil (with a renewal cycle of hundreds of years). Therefore, the preparation of agricultural wastes into biochar can solve the environmental hazards caused by agricultural wastes and improve the utilization of shelved resources, as well as be used for carbon capture and carbon sequestration for a long time. This chapter will introduce the techniques for production and modification of biochars derived from agricultural wastes, summarize the common methods for evaluation of biochar's ability for carbon sequestration, demonstrate the current practices and associated mechanisms of using biochar to entrap soil carbon, discuss the factors that impact biochar's ability for carbon sequestration, and finally present some potential research trends in the field.

10.2 Preparation of Agricultural Waste-Based Biochar (AWB)

As summarized above, the abundance of lignin, cellulose, and hemicellulose in agricultural wastes and their easy accessibility make them excellent raw materials for the preparation of biochar. It is estimated that 500 million tons of agricultural waste of plant origin can be generated globally each year (Duque-Acevedo et al. 2020).

The methods of converting biomass to biochar include torrefaction, pyrolysis (including fast pyrolysis, slow pyrolysis, flash pyrolysis, and microwave-assisted pyrolysis), gasification, combustion, and hydrothermal carbonization. Abhishek et al. introduced the differences between these preparation methods in detail (Abhishek et al. 2022). Among them, pyrolysis is the most common and convenient method for biochar preparation. The biomass type and the pyrolysis temperature have exerted a most significant influence on the individual properties of biochar in this method. Table 10.1 summarizes the effects of different agricultural waste feedstocks and pyrolysis conditions on the key properties of biochar. In general, the surface area, micropore volume, and hydrophobicity are positively correlated with the carbon content of biochar.

Wood-based agricultural wastes, such as trees and their residues, have low moisture content, low ash content, and high bulk density. In contrast, non-wood-based agricultural wastes (crop residues, animal manures, etc.) have the opposite characteristics. Moisture content would increase the energy required for the pyrolysis process and also inhibit the formation of the carbon skeleton of biochar. Darmstadt et al. found that with the decrease in moisture content of maple bark, the prepared biochar formed more polycyclic aromatic hydrocarbons and graphite structures (Darmstadt et al. 2000).

The content of lignin, cellulose, and hemicellulose in agricultural waste also has a significant effect on the formation of biochar. Cellulose and hemicellulose contribute to tar formation because they can decompose at temperatures below 450 °C. However, lignin has strong resistance to thermal decomposition and therefore prefers to form carbon skeletons. Shariff et al. found that the content of cellulose (39.05%) and hemicellulose (22.49%) was higher in coconut leaves than in coconut husk (33.61% and 22.03%, respectively), and the content of lignin in a coconut shell (28.22%) was higher than that of coconut leaves (21.46%) (Shariff et al. 2016). Thus, the pyrolysis of coconut husks lead to a higher biochar yield than the leaves, and the husk-derived biochar was higher in carbon content and more hydrophobic.

The differences in agricultural waste feedstock also bring divergence in surface area, pore volume, and pH for biochar. In a study of Apaydın-Varol and Pütün, it was found that pine cone biochar (1.80 $m^2\ g^{-1}$) and peanut shell biochar (2.02 $m^2\ g^{-1}$) had higher surface area than soybean cake biochar (0.52 $m^2\ g^{-1}$) and corn stover biochar (0.76 $m^2\ g^{-1}$) (Apaydın-Varol and Pütün 2012). The high content of inorganic matter (ash) in agricultural waste became an important factor in weakening the surface area of biochar. The ash content of herbaceous biochar is higher than that of woody biochar, which results in more pores of the former being blocked by ash. This makes the surface area and pore volume of herbaceous biochar significantly

Table 10.1 Physicochemical characteristics of biochar from agricultural waste at varying pyrolysis temperature

Feedstock	T (°C)	pH	Surface area (BET) (m^2 g^{-1})	Pore diameter (nm)	Pore volume (cm^{-3} g^{-1})	Ash (%)	Element content (%)				References
							C	H	N	O	
Vegetable waste	200 °C for 2 h	5.95	0.36	2.59	43.24	16.59	52.89	6.90	4.20	36.02	Igalavithana et al. (2017)
Vegetable waste	500 °C for 2 h	11.23	50.26	3.22	54.61	36.67	74.71	3.08	5.41	16.81	
Pine cone	200 °C for 2 h	4.15	0.47	2.38	45.13	0.77	69.74	2.13	1.03	27.09	
Pine cone	500 °C for 2 h	6.77	192.97	10.2	2.44	8.96	74.64	2.62	1.81	20.94	
Pitch pine wood chips	300 °C fast pyrolysis	–	2.9	–	–	4.5	63.9	5.4	0.3	30.4	Kim et al. (2012)
Pitch pine wood chips	400 °C fast pyrolysis	–	4.8	–	–	7.9	70.7	3.4	0.4	25.5	
Pitch pine wood chips	500 °C fast pyrolysis	–	175.4	–	–	7.7	90.5	2.5	0.3	6.7	
Wheat-straw	400 °C for 1.5 h	8.2	10	4.6	0.012	11	57.8	3.2	1.5	21.6	Gai et al. (2014)
Wheat-straw	500 °C for 1.5 h	8.3	111	3.3	0.09	11	70.3	2.9	1.4	17.7	
Wheat-straw	600 °C for 1.5 h	9.2	177	2.5	0.11	12	73.4	2.1	1.4	14.9	
Wheat-straw	700 °C for 1.5 h	9.2	107	2.2	0.058	15	73.9	1.3	1.2	14.6	
Corn-straw	400 °C for 1.5 h	10.2	4	8.1	0.008	14	56.1	4.3	2.4	22.0	
Corn-straw	500 °C for 1.5 h	10.4	6	2.1	0.012	17	58.0	2.7	2.3	21.5	

Corn-straw	600 °C for 1.5 h	10.4	7	6.3	0.012	18	58.6	2.0	2.0	18.7	
Corn-straw	700 °C for 1.5 h	10.4	3	8.2	0.006	18	59.5	1.5	1.6	16.6	
Peanut-shell	400 °C for 1.5 h	9.3	5	5.2	0.007	9	58.4	3.5	1.8	21.0	
Peanut-shell	500 °C for 1.5 h	9.4	28	3.2	0.022	10	64.5	2.8	1.7	18.5	
Peanut-shell	600 °C for 1.5 h	9.6	185	2.4	0.110	11	71.9	2.0	1.6	15.0	
Peanut-shell	700 °C for 1.5 h	9.9	49	2.7	0.033	12	74.4	1.4	1.4	14.2	
Wood	850 °C for 3 h	–	172	–	0.121	6.3	44.24	6.05	0.86	41.60	Ng et al. (2017)
Chicken manure	850 °C for 3 h	–	342	–	0.224	25.3	28.2	3.5	8.1	33.8	
Yak manure	300 °C for 3 h	7.6	3.6	11.3	0.010	17.8	41.6	1.9	3.2	27.4	Zhang et al. (2018a)
Yak manure	500 °C for 3 h	–	17.3	7.5	0.033	19.83	41.3	1.7	3.0	24.4	
Yak manure	700 °C for 3 h	11.8	82.9	3.6	0.074	21.35	41.2	1.4	2.7	20.7	
Pig manure	500 °C for 4 h	10.4	31.57		0.044	51.7	47.7	1.91	2.49	–	Xu et al. (2016)
Wheat straw	500 °C for 4 h	9.84	20.20		0.041	21.7	60.5	2.31	0.97	–	

lower than those of woody biochar. Yuan et al. found that the pH values of corn straw biochar, peanut biochar, and soybean biochar prepared at 300 °C were 9.4, 8.6, and 7.7, respectively, showing alkaline characteristics (Yuan et al. 2011). In contrast, the pH of rape straw biochar was acidic (6.5). The researchers hypothesized that the alkaline substances released by the formed biochar are different due to different sources of agricultural waste (Yuan et al. 2011). In addition, the amount of –COOH and –OH formed during the pyrolysis of biochar from different sources also differed. This is an important reason for the pH difference of biochar.

Pyrolysis temperature is another key factor that affects the properties of biochar. The decomposition and volatilization of organic matter in the agricultural waste can be improved with the increase in pyrolysis temperature. This contributes to the formation of micro-pores and the increase in the surface area of biochar. Pyrolysis can gradually degrade cellulose and lignin, which can solidify vascular bundles or form channel structures to increase the surface area and pore volume of biochar. High temperatures can induce the conversion of lignin into polycyclic aromatic hydrocarbons, resulting in stronger hydrophobicity and thermal stability of biochar. When the pyrolysis temperature increases to 350–650 °C, the original chemical bonds of biomass will be broken and reorganized to form new functional groups. In addition, the dehydration of biomass during pyrolysis leads to low content of H- and O-containing functional groups in biochar. The surface functional groups can be used as both electron acceptors and electron donors. Therefore, it leads to the formation of coexisting areas whose properties can range from acidic to basic and from hydrophilic to hydrophobic.

The yields of biochar vary according to the classification of the pyrolysis rate of the agricultural waste. For example, heating times of >5 min to several hours, 10–25 min, and <1 min were classified as slow (0.1–10 °C s^{-1}), fast (10–200 °C s^{-1}), and flash (>1000 °C s^{-1}) pyrolysis, respectively. The yield of biochar under these three mode conditions ranges from 25–50%, 15–25%, and 5–15%, respectively. Of course, the properties of biochar, such as carbon content, ash content, type and content of functional groups, and soluble organic matter, are largely related to the pyrolysis temperature in the preparation (Table 10.1). In general, as the pyrolysis temperature increases, the content of H and O elements in the finished biochar gradually decreases. Correspondingly, the content of C and N is increased. Al-Wabel et al. investigated the effect of the change in pyrolysis temperature on the properties of biochar (Al-Wabel et al. 2013). The results showed that the yield of biochar decreased over temperature, which were $51.33 \pm 2.38\%$, $31.86 \pm 1.19\%$, $27.22 \pm 0.57\%$, and $23.19 \pm 0.65\%$ at the peak pyrolysis temperature of 200, 400, 600, and 800 °C, respectively. In addition, the porosity and the content of aromatic carbon of biochar were proportional to the pyrolysis temperature. Besides, the biochar yields are largely determined by the composition of major lignocellulosic biomass at specific temperatures, for example, biomass with higher lignin content corresponded to greater biochar yield and carbon content of biochar.

10.3 Common Biochar Modification Methods for Improved Fixation of GHG

Despite excellent advantages of biochar, there are still some limitations when it is applied to the actual environment, such as insufficient surface area and pores, poor affinity for most anionic metals, and unpromising adsorption efficiency for some inert organic pollutants. The molecular kinetic diameter of CO_2 is 0.33 nm, so micropores (<1 nm) are the main sites of CO_2 adsorption (Feng et al. 2021). However, microporosity alone cannot achieve high CO_2 adsorption capacity of biochar and requires biochar to have a suitable pore structure. Macropores and mesopores are the channel for CO_2 diffusive, which can promote CO_2 adsorption in micropores. As polar and acidic molecules, the fixation of CO_2 on basic and polar functional groups is prominent. Therefore, targeted surface modification and activation of biochar becomes increasingly important in order to improve the properties and applications of biochar. Currently, the common modification methods can be divided into physical, chemical, and biological methods.

10.3.1 Physical Method

Physical modification is mainly to improve the pore structure of biochar and increase the number of micropores and mesopores. Through such modification, the specific surface area of biochar can be increased, and oxygen-containing functional groups can be introduced to the surface and interior of biochar. Physical modifications can also enhance the performance of biochar by improving the surface variable chemical properties of biochar; therefore, the properties are easy to control. At present, the relatively mature physical modification methods include steam method, ball milling method, microwave method, etc. For example, by using a mixture of high temperature CO_2 and ammonia to modify cotton stalk biochar, CO_2 will be able to thermally etch the biochar to produce rich microporous structure. At the same time, N_2 formed under high temperature can be loaded onto the biochar to form nitrogen-based functional groups. Compared with the original biochar, the elevated number of microporous structures in the modified biochar can significantly increase its CO_2 adsorption capacity.

10.3.2 Chemical Modification

Chemical modification is to modify the biochar using activators such as acids, bases, hydrogen peroxide, metals, and/or metal oxides. Chemical modification can change the surface chemical structure of biochar to give it more functional groups, microporous structure, larger specific surface area, and cation exchange capacity. These modifications have greatly changed the structure and properties of AWB and improved its adsorption and capture capacity for CO_2, N_2O, and CH_4. In addition, chemical modification can effectively eliminate unfavorable impurities of AWB and improve the surface functional group ratio and pore structure of AWB. For example, using phosphoric acid to impregnate and activate biochar can form phosphate and polyphosphate cross-bridges in the internal pore structure of biochar. This can effectively avoid the collapse of biochar pores due to excessive shrinkage during formation. Abundant pore structure can provide excellent structural basis for AWB to fix CO_2 and CH_4. Alkali-modified biochar has higher aromaticity and N/C ratio. This will affect the redox state of the soil, thus improving the ability of AWB to capture CO_2. The doping of nonmetallic elements (N, S, B, P, etc.) into biochar can significantly improve the electron transfer capacity of biochar, thereby enhancing its adsorption capacity for CO_2 and CH_4. The doping of N element can easily form nitrogen functional groups on the surface of AWB, which greatly improves the affinity of AWB for CO_2.

10.3.3 Biological Modification

The biological method uses microorganisms to convert organic matter into biogas and digestate and then obtain biochar from the digested residues of microorganisms. The digested biochar exhibits excellent properties such as higher specific surface area and pH value and stronger anion exchange capacity. Biochars with high redox activity can promote bacterial growth through direct interspecies electron transfer and activate the coprophilic oxidation of organic matter that acts as an electron donor during anaerobic fermentation. Compared with virgin biochar, biochar prepared from nitric acid exhibited better redox capacity. This change is very beneficial for AWB to fix CH_4. The N^{-5} or N^{-6} of biochar are converted to nitrogen oxides during the biological modification, and these nitrogen oxides are considered to be the preferred electron acceptors for anaerobic respiration by microorganisms. Therefore, this type of biochar can effectively inhibit the activity of some bacteria and achieve carbon sequestration.

10.4 Evaluation of Biochar for Soil Carbon Sequestration

10.4.1 The Capacity of AWB for Carbon Sequestration in Soil

Compared with other carbon sequestration technologies, biochar is a more efficient and sustainable carbon sequestration method. After biochar is applied to soil, its own excellent adsorption properties and porous structure can improve the efficiency of adsorption and sequestration of greenhouse gases in soil. Besides, the stable carbon skeleton structure of biochar is very difficult to be decomposed, which leads to its long-term existence in the soil as a carbon sink. Therefore, the “carbon sequestration and emission reduction” (CSER) function of biochar gives it a new vitality and mission, in addition to the soil quality improvement and contaminated soil remediation as a soil amendment.

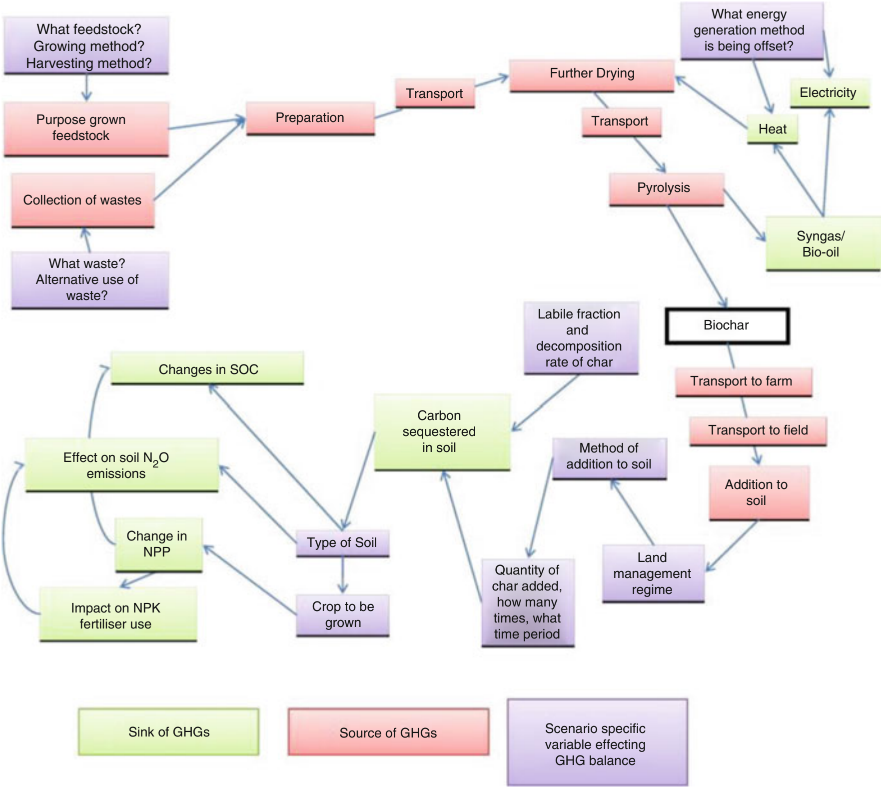

Fig. 10.3 Influencing factors and processes in the life cycle assessment (Hammond et al. 2011)

Lehmann et al. compared the residual amount of biomass directly decomposed in soil with the carbon retention amount after converting biomass into biochar (Lehmann et al. 2006). The results showed that about 50% of the initial carbon storage could be maintained after biomass was converted into biochar. In addition, the researchers estimated that biochar could reduce 20.1–34.9 × 10^9 t a^{-1} of CO_2 for the global environment by 2100, if extrapolated from the current CSER capacity of biochar of 1.28–1.36 × 10^9 t a^{-1}. Woolf et al. used the BGRAM model to analyzed the impact of biochar on greenhouse gas (CO_2, CH_4, and N_2O) emissions in soil (Woolf et al. 2010). The simulation results showed that the biochar converted from agricultural and municipal wastes was capable of fixing up to 1.8 Pg CO_2-equivalent (CO_{2e}) of carbon per year. This accounted for 12% of the total global greenhouse gas emissions. The ability to store a cumulative total of 130 Pg CO_{2e} over 100 years through the use of biochar showed an even greater carbon storage capacity. Hammond et al. investigated the CSER capacity of ten different AWB in soil (Hammond et al. 2011). The researchers comprehensively considered all the influencing factors of biochar throughout its whole life cycle (Fig. 10.3). The results showed that biochar formed from each ton of biomass feedstock exhibits a CSER

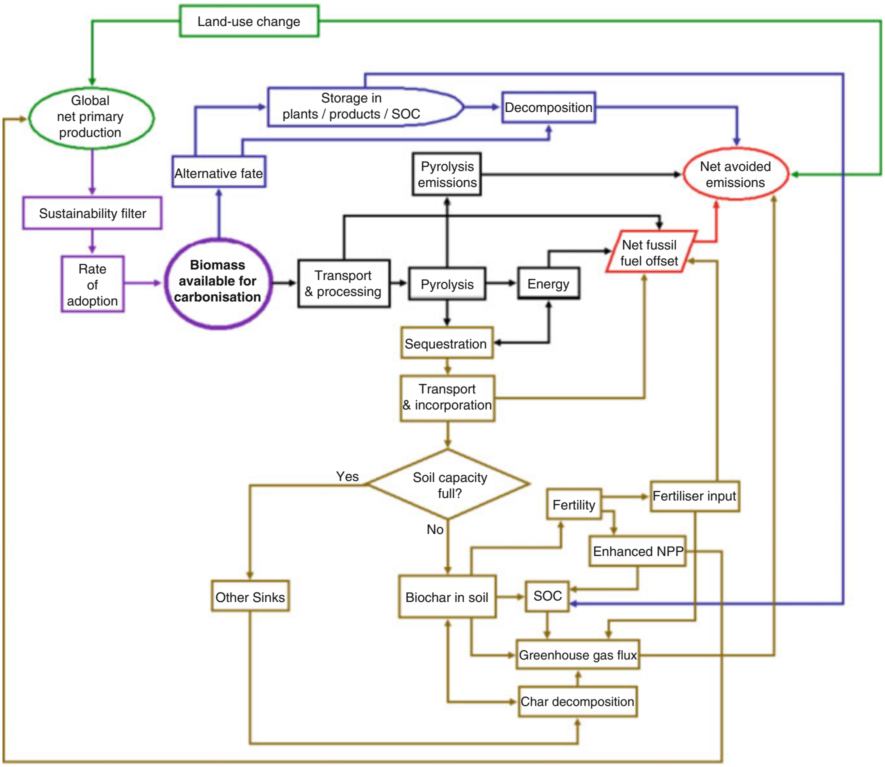

Fig. 10.4 Schematic of biochar greenhouse gas assessment model, BGRAM 1.0

potential of 0.7–1.3 t CO_{2e}, showing a greater carbon storage advantage than other biomass technologies.

10.4.2 The Assessment Methods of CSER Capacity of Biochar

The CSER of biochar is a complex process, and each procedure is interconnected. This close linkage leads to a multiplicity assessment of biochar. Woolf et al. developed a BGRAM 1.0 model to evaluate the CSER of biochar for greenhouse gases (Fig. 10.4) (Woolf et al. 2010). The researchers concluded that agricultural wastes can be pyrolyzed to form stable biochar, which can prevent biomass from being decomposed immediately. The energy input from the pyrolysis process can offset part of the CH_4 and N_2O emissions. In addition, biochar, when added to the soil, can improve the ability of soil to maintain water and nutrients, leading to increased plant growth. This is a positive feedback effect on the removal of CO_2 from the atmosphere. Also, biochar in the soil decays slowly during long-term tillage or transport activities, returning small amounts of CO_2 to the atmosphere. These processes can be well assessed using the BGRAM 1.0 model.

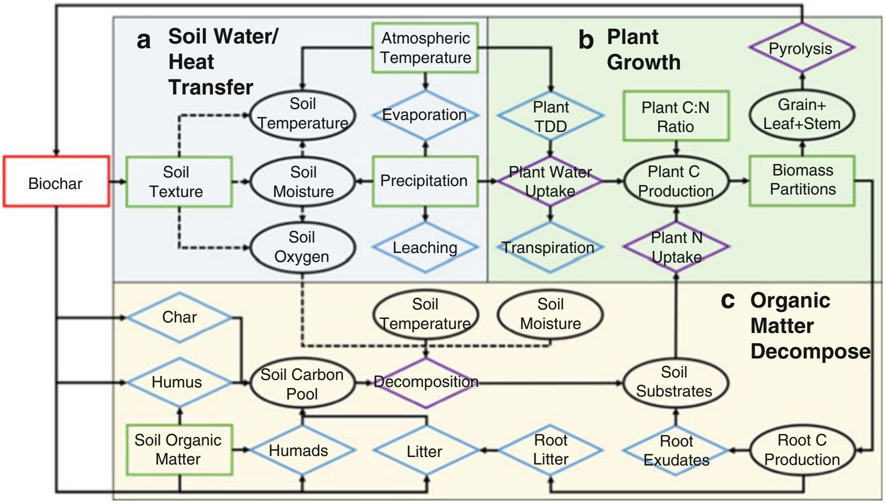

Fig. 10.5 Concepts and algorithmic processes for Biogeochemical Field (BGCF), including (**a**) "Soil Water/Hear Transfer" module, (**b**) "Plant Growth" module, and (**c**) "Organic Matter Decompose" module

Responses of soil climate to biochar is the fundament for analyzing the mechanisms of carbon sequestration; therefore, Yin et al. proposed a biogeochemical field model to generalize and illustrate the process of carbon sequestration of biochar in soil (Fig. 10.5) (Yin et al. 2022). The researchers believed that in this model, the "Soil Water/Heat Transfer" module is considered to account for the changes in water transport and heat transfer in soil after the addition of biochar and thus calculate the spatial and temporal distribution of soil temperature. In the "Plant Growth" module, biochar interacts with plants through three ways: (1) biochar regulates plant exposure to water, heat, and nitrogen stress, thus determining the daily growth of plants; (2) changes in the amount of rhizosphere exudates caused fluctuations in soil carbon supply and affected the stability of organic minerals; (3) after the plant withers or is harvested, the root system becomes a source of replenishment of the SOC pool, activating microorganisms and thus stimulating biochar decomposition. In the "Organic Matter Decompose" module, the change trend of soil matrix is mainly the consideration of the influence of bioavailable C and N (DOC, NH_4^+ or NO_3^-) on microbial activities.

By calculating the total carbon sequestration and total carbon emission of biochar, and considering the energy input and output during in the whole life cycle of CSER of biochar, the CSER capacity of biochar can be deduced. Life cycle assessment (LCA) is a common and relatively mature way to estimate CSER capacity of biochar. Based on the LCA, the following greenhouse gas balance model and energy balance model can be obtained.

First, the equilibrium model of carbon sequestration can be expressed by the following three equations.

$$P_{\mathrm{CO_{2e}}} = \sum\nolimits_i R_i\,(\mathrm{CO_{2e}}) - \sum\nolimits_i E_j\,(\mathrm{CO_{2e}}) \tag{10.1}$$

$$R_{\mathrm{CO_{2e}}} = R_{\mathrm{BC}} + R_{\mathrm{energy}} + R_{\mathrm{plant}} + R_{\mathrm{fertilizer}} + R_{\mathrm{N_2O}} + R_{\mathrm{SOC}} + R_{\mathrm{CH_4}} \tag{10.2}$$

$$E_{\mathrm{CO_{2e}}} = E_{\mathrm{collect}} + E_{\mathrm{trans}} + E_{\mathrm{PC}} + E_{\mathrm{application}} \tag{10.3}$$

In Eq. (10.1), $P_{\mathrm{CO_{2e}}}$ is the net carbon sequestration of biochar throughout the whole life cycle. $R_i(\mathrm{CO_{2e}})$ and $E_j(\mathrm{CO_{2e}})$ are the total carbon sequestration and carbon emissions of biochar throughout its whole life cycle, respectively. In Eq. (10.2), $R_{\mathrm{CO_{2e}}}$ is the source of carbon sequestered of biochar during the whole life cycle. R_{BC} is the carbon sequestered during biochar preparation, R_{energy} is the reduced carbon emission by replacing fossil energy with by-products formed during biochar production, R_{plant} is the additional carbon absorbed by stimulating plant growth after applying biochar, $R_{\mathrm{fertilizer}}$ is the reduced carbon emission by reducing other fertilizer inputs after using biochar, $R_{\mathrm{N_2O}}$ is the reduced carbon emission by suppressing soil N_2O emission, R_{SOC}, is the reduced carbon emission by suppressing soil SOC decomposition, and $R_{\mathrm{CH_4}}$ is the reduced CH_4 emission by preparing livestock and poultry manure-based agricultural waste into biochar. In Eq. (10.3), $E_{\mathrm{CO_{2e}}}$ is the total carbon emissions of biochar during the whole life cycle. E_{collect} is the carbon emissions during the collection of agricultural waste. E_{trans} is the carbon emissions during the transportation of agricultural waste and biochar. E_{PC} is the carbon emissions during the construction of facilities required for biochar preparation and the pyrolysis of agricultural waste, and $E_{\mathrm{application}}$ is the carbon emissions during the site use of biochar.

Second, the energy balance model in the sequestration process can be expressed by the following two equations.

$$P_{\mathrm{energy}} = e_{\mathrm{syngases}} - \sum\nolimits_i e_{j(\mathrm{input})} \tag{10.4}$$

$$e_{\mathrm{input}} = e_{\mathrm{collect}} + e_{\mathrm{trans}} + e_{\mathrm{PC}} + e_{\mathrm{application}} \tag{10.5}$$

In Eq. (10.4), P_{energy} is the energy balance value throughout the whole life cycle of biochar. e_{syngases} is the production potential of biomass gas energy, and $e_{j(\mathrm{input})}$ is the energy input at each stage of the whole life cycle of biochar. In Eq. (10.5), e_{collect} is the energy input during the collection of agricultural waste. e_{trans} is the energy input during the transportation of agricultural waste and biochar. e_{PC} is the energy input during the construction of facilities required for biochar preparation and the pyrolysis of agricultural waste, and $e_{\mathrm{application}}$ is the energy input during the site use of biochar.

Feng et al. used this method to estimate the CO_2 sequestration capacity of three types of biochar prepared from agricultural waste (Feng et al. 2020). The results showed that the net sequestration of greenhouse gases by straw biochar, livestock manure biochar, and wood biochar were 4.51×10^8, 4.18×10^8 and 2.66×10^8 of CO_{2e}, respectively. Although there were differences in the greenhouse gas sequestration capacity of biochar prepared from different sources of agricultural wastes, all of them showed positive CSER effects. In addition, based on the types, sources, and distribution of agricultural wastes, the researchers estimated that the proportions of CSER of these three types of biochar were 31.41%, 29.11%, and 18.52%, respectively (the other 20.96% came from biochar prepared from municipal organic waste). Straw biochar showed the best CSER potential.

Woolf et al. developed a model for carbon fixation of biochar in soil, which is based on the guidelines issued by IPCC (Woolf et al. 2021). The model expands the scientific background and expands the default coefficient related to greenhouse gas flux. The optimization of these conditions can reduce the error of model estimation when users have more detailed biochar information. The model is presented in the form of Eq. (10.6).

$$\mathrm{GHG}_{\mathrm{bc}} = M_{\mathrm{bc}} \cdot F_{\mathrm{C}} \cdot F_{\mathrm{perm}} \cdot 44/12 + 0.23 \cdot n \cdot \mathrm{GWP}_{\mathrm{N_2O}} \tag{10.6}$$

where $\mathrm{GHG}_{\mathrm{bc}}$ is the greenhouse gas emissions ($\mathrm{CO}_{2\mathrm{e}}$) reduced by adding biochar to soil. M_{bc} is the mass of biochar added to the soil. F_{C} is the organic carbon content of biochar, and its value can be obtained from Eq. (10.7). F_{perm} is the proportion of organic carbon in biochar 100 years later. 44/12 is the conversion factor from carbon to $\mathrm{CO}_{2\mathrm{e}}$. n is the baseline annual $\mathrm{N_2O}$ emissions from the total area of land over which biochar is applied at an application rate in excess of 10 Mg C ha^{-1}. $\mathrm{GWP}_{\mathrm{N_2O}}$ is the global warning potentials of $\mathrm{N_2O}$, and its value can be viewed through IPCC.

$$F_{\mathrm{C}} = F_{\mathrm{C,daf}}(1 - F_{\mathrm{a,bc}}) \tag{10.7}$$

where $F_{\mathrm{C,daf}}$ is the organic carbon content of biochar on a dry ash-free basis. This parameter is a regression function of the pyrolysis temperature of biochar. Its value is $0.93–0.92\mathrm{e}^{-0.0042T}$, and T is the pyrolysis temperature of biochar. $F_{\mathrm{a,bc}}$ is the ash content of biochar, and their values can be obtained by Eq. (10.8).

$$F_{\mathrm{a,bc}} = \frac{F_{\mathrm{a,bm}}}{F_{\mathrm{a,bm}} + Y_{\mathrm{bc}}} \tag{10.8}$$

where $F_{\mathrm{a,bm}}$ is the ash of biomass. Y_{bc} is the yield of biochar produced by pyrolysis, with a value of $0.126 + 0.5391\mathrm{e}^{-0.004T} + 0.002733L$. L is the content of lignin in raw materials.

Therefore, in this model, the researchers comprehensively considered the use amount of biochar, application years, scope of action, pyrolysis temperature, and other factors and estimated the persistent carbon fixation behavior and effect of AWB applied to soil. It should be noted that the two parameters in this model, F_{C} and F_{perm}, are summarized based on the published literature. Therefore, the accuracy of these two parameters is restricted.

10.5 Biochar's Ability for Soil Carbon Sequestration

10.5.1 Original Biochar

Biochar can adsorb gas molecules through van der Waals forces, and this process is closely related to the specific surface area, pore size distribution, pore volume, and surface hydrophobicity of biochar.

Woolf et al. suggested that biochar applied to soil could achieve long-term carbon sequestration and reduce greenhouse gas emissions (Woolf et al. 2010). The authors believed that biochar had a highly stable structure after high-temperature pyrolysis and could be combined with and fixed CO_2 after being put into soil. Leng et al. also reported that the addition of biochar to soils could alter the aeration properties of soils, thereby reducing CH_4 emissions to the atmosphere (Leng et al. 2012).

Biochar after high-temperature pyrolysis has abundant pore structure, which provides an excellent physical basis for the adsorption and fixation CO_2 by biochar. Macropores and mesopores contribute to the diffusive transport of CO_2 molecules, while micropores provide adsorption sites as direct storage sites for CO_2. Therefore, the reasonable construction of graded pores can effectively enhance the performance of biochar in capturing CO_2. Cao et al. prepared biochar with different straw and wood as raw materials to study its adsorption performance on CO_2 (Cao et al. 2022). The results showed that wood-based biochar had better adsorption capacity for CO_2, because the pore structure and surface area of wood-based biochar were better than those of straw-based biochar.

Lefebvre et al. prepared the corresponding biochar using sugarcane bagasse and investigated its ability to sequester carbon from soil (Lefebvre et al. 2020). The researchers found that the addition of biochar was able to lead to a steady increase in the storage of soil carbon. The RothC model simulated the use of bagasse biochar for 20 years to sequester at least 9.1 Mt of CO_2 for a 5.77 Mha sugarcane field in São Paulo State. In addition, the researchers also found that the emissions of N_2O, another greenhouse gas in the soil, decreased by $28 \pm 16\%$ after 1 year of biochar application. The researchers concluded that the addition of biochar affected the nitrification and denitrification processes in the soil, and biochar increased the water holding capacity of the soil. This reduced the demand for nutrients in soil, which in turn reduced the loss of N.

10.5.2 Activated/Modified Biochar

Biochar exhibits good affinity for CO_2 through its excellent structure and surface properties. Through targeted activation or modification, the properties of biochar can be further enhanced, and the CSER capacity can be improved.

Igalavithana et al. prepared biochar using pine wood chips and steam activated it at 550 °C for 45 min (Igalavithana et al. 2020). The results showed that pine wood chip biochar exhibited a higher adsorption capacity for CO_2 due to its higher surface area and microporosity than sludge biochar. In addition, the surface area, microporous structure, and oxygenated basic functional groups of pine wood chip biochar were further enhanced after steam activation, and the adsorption performance of CO_2 was increased by 8.96%.

The adsorption and sequestration of CO_2 by biochar are influenced by the chemical properties of the biochar surface. Many study results have shown that the introduction of nitrogen-containing functional groups can increase the alkaline sites on biochar and enhance the adsorption capacity of CO_2. Some specific activators, such as NaOH, KOH, and K_2CO_3, can dissolve the soluble ash, lignin, or cellulose inside the biochar during the activation process, thus increasing the oxygen-containing functional groups and alkaline groups of the biochar. He et al. used chitosan as an N source for surface modification of rice husk biochar and activated the modified biochar by KOH and then used it for CO_2 fixation (He et al. 2021). The researchers found that the CO_2 adsorption capacity of the activated biochar was significantly higher than that of the original one. They attributed this phenomenon to the elevated surface area and micropore volume of the biochar due to the activation of KOH, as well as the doping of N elements.

Wu et al. used KOH to activate corn kernel biochar at different mass ratios and temperatures in N_2 atmosphere and investigated its effect on CO_2 fixation (Wu et al. 2021). The results showed that the activated biochar was able to expand the internal pore structure and the porosity increased with the increase of KOH/biochar mass ratio. KOH was injected into the micropores of biochar under high temperature and then expanded the pore structure by chemical reactions and changed the surface functional groups. Pyrolysis at 900 °C was able to greatly increase the number of ultramicropores (<0.7 nm) and the content of oxygen functional group (45.5%) of biochar. In addition, the researchers found that the activated biochar exhibited stronger affinity for CO_2 (3.63 mmol g^{-1}) than N_2 (0.13 mmol g^{-1}). This was mainly due to the fact that CO_2 had a higher quadrupole moment than N_2, which made it easier for CO_2 to form van der Waals forces with the polar regions of the biochar. The researchers also indicated that higher KOH content and temperature can destroy part of the original amorphous structure of biochar, which could have some negative effects on the adsorption of CO_2.

Lahijani et al. prepared biochar by using walnut shells pyrolyzed at different temperatures and impregnated the biochar with alkaline metals and finally further heat treated under N_2 atmosphere (Lahijani et al. 2018). This study led to the conclusion that at 25 °C and 1 atm pressure, the Mg-loaded biochar (900 °C pyrolysis) adsorbed more CO_2 (82.0 mg g^{-1}) than the unmodified and inactivated biochar (72.6 mg g^{-1}). The alkali metals loaded onto the biochar can form alkaline metal ion groups by pyrolysis under anaerobic conditions and then capture CO_2 through chemical interactions. The abundant pore structure formed in walnut shells biochar during high-temperature pyrolysis, and the optimization of microporous structure and surface area during activation made the biochar exhibit strong affinity for CO_2. The researchers concluded that although physical and chemical interactions played a synergistic role in CO_2 adsorption and immobilization, physical adsorption remained the main controlling mechanism for CO_2 adsorption. Compared with the biochar modified by Al, Fe, Ni, Ca, and Na, Mg-modified biochar showed the best stability and rapid cycle regeneration performance for CO_2 capture.

Xu et al. prepared the corresponding biochar using wheat straw and pig manure under anaerobic conditions (Xu et al. 2016). The researchers found that the CO_2 sequestration by wheat straw biochar (34.4 mg g^{-1}) was better than that by pig manure biochar (23.5 mg g^{-1}) at 25 °C. The trend was not consistent with the changes in surface area and pore volume of biochar. Physisorption and chemisorption together dominated the CO_2 sequestration on biochar. The researchers believed that the alkali metals (K, Na, Ca, Mg) and their carbonates in biochar were able to form alkaline adsorption sites on the surface layer of biochar during pyrolysis. This contributed to the adsorption and sequestration of CO_2 by biochar. This was similar to the results of Lahijani et al. (2018). In addition, the researchers found that the heat of adsorption of CO_2 on both biochars gradually increased with the increase in the temperature of the adsorption environment. This proved that CO_2 prefers to be physic-adsorbed on biochar at low temperature environment, while chemical adsorption was dominant at high temperature.

10.6 The Mechanisms Associated with Carbon Sequestration in Soil by Biochar

Biochar-based carbon sequestration in soil are enabled by the adsorptive retention of greenhouse gases, the remarkably lower carbon decomposition rates in soil due to the recalcitrant nature of biochars, as well as the biochar-induced biogeochemical changes of soils that can alter the production and oxidation processes of greenhouse gases. On the one hand, the carbon-enriched biochars can maintain majority of carbon in pristine biomasses, which would otherwise be decomposed and released into atmosphere to a very considerable extent once applied in soil. Instead, the carbons in biochar especially prepared at high temperatures are dominated by stable condensed aromatic carbon structure, which usually decompose at a very low rate. Compared to natural biomasses that can decay in months to a few years, the biochars can retain for hundreds to thousands of years, which significantly reduces carbon emission into atmosphere. Meanwhile, biochars have rich and well-developed pore structure and surface area after high-temperature pyrolysis. The macropores and mesopores in biochar can provide channels for diffusion of gases and accommodate CO_2, CH_4, etc. in the soil. Compared with soil colloids and organic matter, biochar exhibits a more substantial surface area, which provides more adsorption sites to sequestration CO_2. Besides, the oxygen-bearing functional groups on the surface of biochar such as –COOH, –OH, and –CO can promote the formation of hydrogen bonds between CO_2 and biochar and thus promote retention of greenhouse gases.

On the other hand, biochar incorporation could inevitably alter the soil carbon processes that result in changes of carbon cycle in soil and even at a global scale. This can be ascribed to the change of soil pH, redox potential, and microbial community, which exerts important influences on elemental cycles in soil. Herein, the major processes associated with biogeochemical cycle of soil organic carbon that can be reshaped as a result of biochar are summarized (Feng et al. 2020).

Firstly, biochar can induce change of soil pH and redox potential. The increased soil pH are usually observed as biochars are applied into soils. This phenomenon is due to the strong alkalinity of biochars, which result from the abundant alkaline metals and functional groups such as nitrogen-containing functional groups including amide, pyrrolic, imide, pyridinic, and lactam groups. As soil pH increases, CO_2 solubility in soil solution becomes enhanced. Thus, a higher soil pH is more favorable for the CO_2 retention in soil, due to greater affinity of biochar and higher solubility of CO_2. Because of this, biochars were impregnated by alkali metals or alkaline-earth metals with an intention to enhance their affinity for CO_2. For example, MgO impregnation increased the adsorption of CO_2. On the other hand, biochar is able to mediate soil redox potential because of the reducing moieties of biochars and biochar-induced changes of soil processes. It was observed in our recent work that a pine wood-derived biochar can always decrease soil pH, not dependent on soil moistures.

Second, biochars can affect the composition and activity of soil microorganisms, thereby changing the mineralization of soil organic carbon and oxidation-reduction of greenhouse gases. It is noted that dissolved organic carbon of biochars can provide carbon and nutrient sources to boost soil microbes, and biochar skeleton serves as habitat for microorganisms. It was reported that biochar accelerated colonization of low carbon turnover bacterial taxa (e.g., *Actinobacteria* and *Deltaproteobacteria*) and the bacterial taxa that stabilize soil aggregates (e.g., *Actinobacteria* and *Acidobacteria*) (Zheng et al. 2018). This greatly enhances carbon sequestration in soil.

The changed soil properties can thus alter the elemental biogeochemical cycles, which may be beneficial for carbon sequestration. The multivalent metals such as iron (Fe) and manganese (Mn) play important roles in mediating carbon cycles. The lower redox potential promoted reduction of Fe^{3+} and Mn^{4+}, which is enhanced by the electron mediating capacity of biochars ascribing to the functional groups and condensed aromatic carbon structure. Biochar could also promote Fe reducing bacteria *Clostridium* sensu stricto *10*, which contributes to Fe^{3+} reduction. The Fe^{2+}/Fe^{3+} cycles can not only reduce the availability of dissolved organic carbon for methanogenesis but also enhance the oxidation of CH_4. Similarly, Mn can drive the reduction of CH_4 and anaerobic oxidation of CH_4 in wetland and dryland systems. Recently, the Fe-induced oxidative radicals are considered to participate in the oxidation of CH_4, but the associated mechanisms are still not well illustrated. Apart from the multivalent metals, the transformation of nitrogen (N), a primary essential nutrient for plant growth, can be affected by biochars. It is acknowledged that biochar could mediate nitrous oxide, an important greenhouse gas, via its influences on N transformation process, such as adsorption of ammonium, (de)-nitrification, and so on. The Fe is also involved in N cycle in which anaerobic ammonium oxidation co-occurs with the iron(III) reduction. This process, called Feammox, resulted in significant formation of nitrogen gas and nitrite. Thus, biochar-induced transformation of multivalent elements is an important pathway to mediate generation of greenhouse gases.

To conclude, the soil carbon cycles can be affected collectively by the soil processes mentioned above. Upon biochar addition, the priming of native soil organic carbon (SOC) occurs, which can enhance the SOC mineralization and evolution of CO_2 at the early stage due to increased labile carbon pool but inhibit production of greenhouse gases from a long-term perspective. The transformation of SOC can be mediated by the soil microbes, which was affected by the biochar. Under most circumstances, SOC co-exists with soil minerals comprising majority of SOC in soil. The association of SOC with common soil minerals such as phyllosilicate minerals and metal oxides such as iron oxides would surely enhance SOC stability and reduce the tendency of SOC to be oxidized, which can be mediated by the biochar addition.

10.7 Factors that Impact Soil Carbon Sequestration Ability of Biochar

10.7.1 Properties of Biochar

The structure and properties of AWB can significantly affect its ability of CSER. For AWB with higher specific surface area and microporous structure, they have higher CSER capability. Because these two provide a better attachment point for AWB to capture CO_2. The well-developed microporous structure of biochar provides good attachment sites for CO_2, while the larger pores become diffusion channels for CO_2. Therefore, wood-based biochar with a higher percentage of micropores has a significantly higher carbon sequestration capacity than straw biochar. The number and type of functional groups on the surface of AWB, especially the basic functional groups, play a key role in the CSER ability of AWB. Basic functional groups, such as amino groups, can easily bind CO_2 molecules. The mineral components of AWB, such as Mg^{2+}, Al^{3+}, and other alkali metals, form alkaline sites after pyrolysis, which have much higher affinity for CO_2 than ordinary fixed sites. In addition to the basic properties of AWB mentioned above, the CSER capacity of AWB is directly related to its own stable carbon content. Generally speaking, as the pyrolysis temperature increases, the content of aliphatic carbon in AWB decreases. The corresponding result is that the content of aromatic carbon in AWB increases, that is, the content of stable carbon becomes higher and higher, which leads to better carbon sequestration of biochar by high-temperature pyrolysis. The amount of AWB can obviously effect on the CSER in soil. In general, with the increase of the use of AWB, its fixation of CO_2 and CH_4 in the soil is gradually increasing.

The content of soluble organic and inorganic carbon in biochar also has a significant effect on its carbon sequestration. Fidel et al. studied the effects of organic carbon and inorganic carbon of corn straw biochar with different treatments on soil CO_2 sequestration (Fidel et al. 2017). The results showed that compared to the original biochar treatment, the CO_2 emissions of soil were significantly higher after the biochar (removed of soluble organic and inorganic carbon) was added to the soil. However, this phenomenon only occurred for a short period of time (≤48 h). This mainly depends on the rapid adsorption and fixation of CO_2 in soil by these unstable inorganic carbon components. After more than 48 h, the unstable inorganic carbon in the biochar was consumed, and then the soil CO_2 capture was mainly by the unstable organic carbon. At the same time, biochar could initiate the natural organic matter in the soil, and these components become the main driving force to help the biochar fix CO_2. Therefore, with the extension of time, the effect of unstable organic carbon and inorganic carbon in biochar on the CO_2 fixed in the soil could be ignored.

The properties of AWB have an obvious influence on CSER. Compared with the original AWB, the modified or activated AWB has more excellent physical and chemical properties. For example, the microporous structure of steam-activated AWB was further increased, which could significantly increase the CO_2 load. The AWB modified by zerovalent iron or alkali metal showed better electron transfer ability. This provided a channel for the modified AWB to rapidly adsorb and fix CO_2.

10.7.2 Soil Properties

The addition of biochar can improve the physical and chemical properties of the soil. This will significantly increase the amount of greenhouse gases fixed in the soil. For example, the expansion of soil pores after AWB is added helps CO_2 and CH_4 diffuse onto the AWB. Increased soil aeration can oxidize CH_4 and reduce CH_4 emissions. The alkaline groups on the surface of biochar can raise the pH of the soil, so that CO_2 can be more easily dissolved in soil water and thus immobilized by biochar. In addition, the increase of biochar addition can improve the dissolution of soluble carbon and activate more organic matter in the soil. These components can provide significant assistance for CO_2 adsorption and fixation by biochar. Sun et al. found that when the field capacity was 70%, the carbon mineralization rate in soil reached its maximum after adding biochar to the soil (Sun et al. 2016). As the temperature increases, the content of mineralized carbon in the soil increases, but at the same time, it would decrease the content of stable carbon and the cycle of carbon cycling. And excessive decrease of soil moisture could inhibit soil respiration by affecting the activity of soil microorganisms, which would reduce the accumulation of soil carbon.

Soil with good nutrient status is more conducive to carbon fixation of AWB. Abundant nutrients can promote plant growth and root micro domain expansion. The growth of plants will absorb more CO_2 from the atmosphere, and the rhizosphere microdomain is conducive to the input of underground carbon. In addition, biochar has a potential role in reducing the decomposition of root secretions and apoplastic matter. The addition of AWB can adjust the population structure and abundance of microorganisms in soil. The weak alkaline soil environment created by AWB will inhibit the reproduction of bacteria, which would lead to the reduction of the decomposition rate of organic carbon in the soil.

10.7.3 Nutrient Management

Some studies found that when biochar was added to the soil, adding chemical or organic fertilizers to the soil at the same time can well reduce carbon transfer and achieve carbon sequestration more effectively (Ngo et al. 2016). The main reason is that the addition of fertilizer can significantly increase the content of available nutrients in the soil. This can effectively promote the growth and development of plants, and with the aid of biochar, plants can absorb and fix more carbon in the atmosphere and soil. Although the mixing of biochar and fertilizer could lead to the release of soluble organic matter in soil. But compared with the fixed amount of carbon, the mixture of biochar and fertilizer showed the phenomenon of emission reduction.

Zhang et al. prepared biochars using waste coffee grounds and wood chips and applied them to the soil as a soil amendment to observe changes in soil carbon pool (Zhang et al. 2018b). The results showed no significant changes in CO_2, N_2O, and CH_4 emissions in the soil after biochar addition. Biochar and fertilizer can activate microbial community activity, which can promote the decomposition of organic matter and release CO_2, N_2O, and CH_4. The volatile organic matter produced during decomposition of organic matter inhibited the digestion process, and this would prevent adequate conversion of NH_4^+ in the soil and be adsorbed by biochar.

10.8 Conclusion and Outlook

The conversion of agricultural waste into environmentally friendly and multifunctional biochar not only solves the problem of environmental pollution caused by waste but also represents an efficient use of shelved resources. In this chapter, the feedstock of agricultural waste and pyrolysis temperature, the two most important factors, on the properties of biochar are summarized. The CSER capacity of biochar and its evaluation methods are discussed and summarized in focus. In addition, the carbon capture and carbon sequestration effects of AWB in soil were evaluated. The carbon capture and carbon sequestration capacity of AWB was mainly related to the surface area, micropore volume, and alkaline function groups of biochar. The influence of biological factors on the CSER of biochar is becoming increasingly important. Through the analysis and discussion of the CSER of biochar, it can be seen that biochar is bound to become one of the superior materials for carbon capture and sequestration in the future, which can greatly mitigate global climate change.

With the continuous deepening of research on AWB, there are some other problems that need to be faced and solved in terms of CSER.

1. The utilization cycle and regeneration mechanism of carbon capture and sequestration of AWB need to be further explored. The carbon sequestration cycle of biochar is a prerequisite for studying its regenerative utilization performance. The regeneration ability of AWB after carbon sequestration is one of the key characteristics of biochar utilization and promotion. Especially, biochar has a

very good affinity for most organic pollutants and heavy metals, so the influence of contaminants on the carbon sequestration effect of AWB should also be a key consideration.

2. The long-term stability of the finished AWB in soil has not been fully demonstrated due to the differences in raw materials and preparation methods of AWB. This property is crucial for the stability and practicality of the carbon sequestration effect of AWB. The techno-economic and environmental feasibility of AWB must be examined from a perspective of system and life cycle.
3. The current research on AWB is mainly focused on pyrolysis, and other preparation methods (flash, hydrothermal, etc.) are not studied in depth. This also has led to the inability to completely and systematically evaluate the CSER potential of AWB.
4. At present, the degree of CSER application of AWB is still in the primary stage, and more potential has not been deeply explored. Effectively activation (physical modification, chemical modification, biological modification, etc.) of AWB for selective adsorption and immobilization of CO_2, CH_4, and other gases should be one of the key directions for future development.
5. Based on the efficient CSER capacity of AWB, the governments and international organizations should develop appropriate technical protocols for AWB application and promote it. This will facilitate the full utilization and further commercialization of different kinds of AWB.

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Contemporary Approaches for Biochar Production from Agro-Waste and Its Current and Prognostic Applications in Environment Health

11

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Abstract

Biochar is produced from the lignocellulosic biomass by pyrolyzing at the temperature range of 550–850 K. Usually, wood residues and agricultural residues are the key feedstocks for biochar production. In recent years, several researchers have focused on biochar preparations toward enhancing physiochemical properties, such as pore volume, specific surface area, pore diameter, electrical conductivity, pH, and ion exchange capacity. Based on its key elements, oxygen, hydrogen, carbon, and nitrogen, and the molar ratios, C/N, O/C, and H/C, biochar has a potential application in environmental purpose. In order to produce a high-valued biochar, technologically improvised methods, such as hydrothermal carbonization, pyrolysis, torrefaction, and gasification, gain significant interest. Besides, biochar is a proven candidate for managing contaminants because of its excellent remediating proficiency. However, some

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limitations still exist that need for further investigations with respect to its properties and applications. In this view, this chapter has been narrated to review with the intention of evaluating different feedstocks (forest/woody/agricultural biomass residue) for their application potential.

Keywords

Biochar · Physiochemical properties · Environmental · Bioremediation · Soil health

11.1 Introduction

In recent times, research communities are showing significant interests on achieving net-zero processes using environment-friendly bioresources, like agro-wastes. Accordingly, agro-residue wastes are considered as most significant since they can be converted to different value-added products. In this context, a thermochemical method, called, pyrolysis, is the most extensive method that involves heating to produce various value-added products, such as gas, biochar, and bio-oil. In general, flash pyrolysis, vacuum pyrolysis, microwave pyrolysis, fast pyrolysis, slow pyrolysis, and hydro-pyrolysis are most widely applied techniques for pyrolyzing the carbon-rich materials to attain biocarbon-related products. These methods are different with respect to their operating temperature, reaction mechanism, pyrolysis method, heating rate, and residence time. Accordingly, based on the required value-added products, the pyrolysis methodology can be selected to proceed. For the instance, vacuum and fast pyrolysis method can favor the production of bio-oil, whereas the hydro-pyrolysis facilitates the production of gases. Studies revealed that the microwave pyrolysis and slow pyrolysis are found to be more favoring and promising to produce the biochar (Nzediegwu et al. 2021). Among the carbon-enriched biomaterials, biochar has extensive applications since it has unique desirable characteristics, such as gross calorific value, specific surface area, structural stability, active functional groups in surface, better cation exchange capacity, and enriched pore volume. Due to its excellent characteristics, biochar is being utilized as wide range of applications, such as adsorbent, microbial fuel cell, catalytic, and gas production, so forth (Li and You 2022). However, the performance of biochar is purely based on its physicochemical properties, which is closely contingent to the pyrolysis method ad conditions. In addition to that, biochar processing methods are interlinked with reactor specifications, nature of feedstock, end-use-applications, and operating conditions. In recent years, there are several reviews that have been made on the production of biochar and its significance. Among them, some significant themes have been summarized in Table 11.1.

While comparing to the available reviews, the present chapter adopts the contemporary approaches for biochar production and its applications toward the positive impacts on environmental beneficiations.

Table 11.1 The recent studies on agricultural residue-based biochar

Sl no	Thematic area	References
1	Production of biochar using different combinations of feedstocks and its uses for removing inorganic and organic pollutants	Ahmed and Hameed (2020)
2	Various strategies for biochar production. The influence of different process parameters on production of biochar	Tripathi et al. (2016)
3	Agro-residue management. Application of biochar for environmental benefits. Importance of slow pyrolysis	Anand et al. (2022)
4	Comparison on fast and slow pyrolysis toward biochar quality. Effect of feedstock composition. Discussion on different parameters for production of biochar	Tan et al. (2021)
5	Studies on categories toward sustainable biochar production. A comprehensive review on crop residues management	Zhu et al. (2022)
6	Influence of physicochemical properties of biochar for the specific applications. Requirements for futuristic research on biochar	Li et al. (2020a, b)
7	Biochar produced from microwave pyrolysis and its characteristic analysis on yield and properties. Discussion on comparison of microwave pyrolysis with other pyrolysis method	Li et al. (2016)
8	Biochar production methods and its integration for soil benefit management. Mechanism of biochar's reaction for soil beneficial applications	Gabhane et al. (2020)

11.2 Feedstock Availability and Characteristics

Feedstocks play important role on production of biochar, which determine the quality and characteristics of the product. The studies revealed that the crop residues exhibit high calorific values, lower ash contents, and compared to organic waste and woody biomass. So far, different crop residues had been potentially exploited as feedstock for production of biochar via pyrolysis. Almost all solid biomass debris act as a promising feedstock for biochar. More than 50 different types of biomass debris have been investigated in research trials, containing a garden and herbal waste, wood, forest and crop residues, animal manure, fruit and vegetable skin, sewage sludge, nut husks, sugarcane bagasse, rice straw, coconut, umbrella trees, and palm husks. Wood and crop residues are the materials for commercial biochar production due to their vast availability and ease of handling. However, differences in density and chemical composition were attained from various species of tree and different stages of growth. Conversion of biochar leads to products with different physical and chemical properties even under the same carbonization conditions due to the different lignocellulose (lignin, hemicellulose, and cellulose) and mineral compositions (K, Si, P, N, S, Ca, Mg, and Na) (Guo 2020). On the other hand, Lee et al. (2013) correlated the ash and moisture content of biochar obtained from sugarcane bagasse, rice straw, coconut, umbrella trees, and palm husks. They showed that rice-straw and coco-peat-derived biochar had the highest ash and moisture content, respectively. In addition, tree trunks of umbrella trees, bagasse of sugarcane, and palm kernel shells

Table 11.2 Feedstock characteristics of different agro-residue-based biomass on dry basis

Feedstock	Moisture content	Fixed carbon	Ash	Volatile matter
Rice husk	0.01	11.44	15.14	73.41
Maize cobs	0	25.51	1.54	72.95
Corncob	0	12.45	5.04	82.38
Sugarcane straw	3.12	3.22	9.17	87.61
Corn stalk	0	14.68	2.91	82.42
Coconut shell	10.10	11.10	3.20	75.50
Cassava rhizome	0	9.08	7.28	83.64
Maize leaves	0	22.73	9.49	67.78
Corn stover	0	8.93	8.86	82.21
Wheat straw	0	9.93	9.37	80.7
Rape stalk	0	7.49	6.42	86.09
Barley straw	2.94	11.83	6.43	78.8
Sugarcane bagasse	7.39	8.87	2.51	81.23
Cassava stem	0	16.07	2.42	81.51
Banana leaves	0	16.92	6.72	84.82
Rice straw	0	10.06	13.07	76.87
Coconut fiber	0	11.10	8.05	80.85

had higher surface area than the biochar of coir peat and rice straw. Another recent study showed that biochar derived (450–650 °C) from willow (*Salix viminalis* L.) had the highest moisture level, ash, and pH compared to pine (*Pinus sylvestris* L.) biochar-derived pyrolysis at 450–650 °C. The properties of biochar discussed above significantly impact soil ecosystems and indirectly affect human health. In this context, the three key factors are considered for the selection of potential feedstock. They are lignocellulosic content, proximate content, and ultimate content. For most of the agro-residues, fixed carbon, ash, volatile mater, and moisture content are observed in the range of 3–26%, 1–15%, 65–90%, and 0–10%, respectively (Table 11.2). In general, volatile matter contents significantly affect the pyrolysis, which impacts the ash content and fixed carbon of the biochar. Commonly, the biochar with high ash content receives more attention as catalyst for thermo-convection. On other hand, such biochar is observed to be undesirable in specific to the use of adsorption process. Normally, agro-residues have low ash contents. Another key factor, fixed carbon, determines the significance of biochar for sequestering atmospheric carbon. Furthermore, the moisture content affects the biochar production, transport, harvest, and storage. Naturally, due to its volume reduction, the lower moisture content favors easy transportation and convenient storage. In addition, lower moisture content supports to attain maximized energy efficiency. Table 11.2 illustrates the characteristics of different agro-residue based biomass on dry basis.

11.3 Pyrolysis Methods for Biochar Production

The pyrolysis method for the agro-residue feedstock must be selected based on the different concerns, such as environmental impacts, energy efficiency, and process economics. In such a way, the six pyrolysis methods are extensively focused, which are microwave, fast, vacuum, flash, slow, and hydro-pyrolysis. Figure 11.1 illustrates the production methodologies for biochar.

Table 11.3 summarizes various types of pyrolysis and corresponding process parameters. In general, slow pyrolysis is executed at low rate of heating (0.1–1 °C s^{-1}) at 300–700 s. During slow pyrolysis, the range of temperature is maintained 300–700 °C. This process can effectively reduce thermal cracking of biomass that favors the condition for formation of biochar. Microwave pyrolysis is a novel method that can produce an efficient biomass conversion. In this method, heat energy is

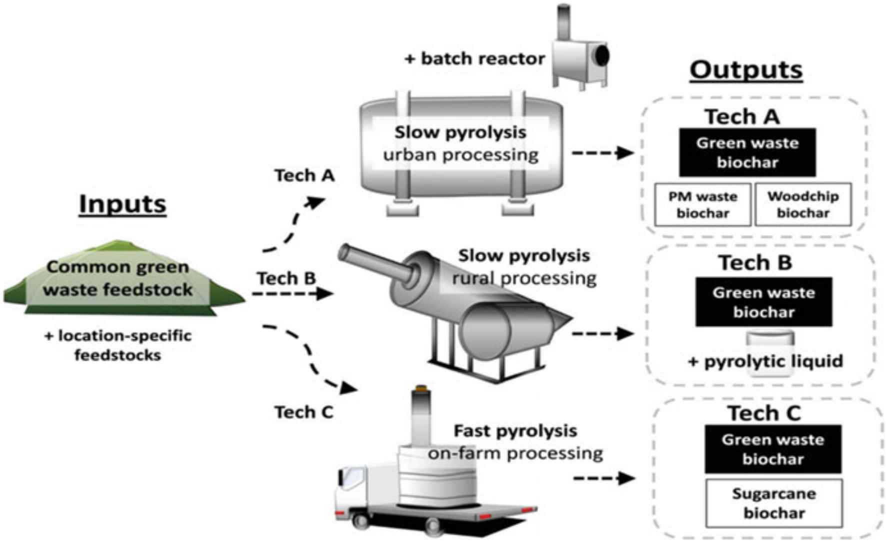

Fig. 11.1 Production methodologies for biochar. (*Adopted from* Allohverdi et al. 2021)

Table 11.3 Various traditional and emerging types of pyrolysis and corresponding process parameters

Pyrolysis method	Residence time (s)	Pressure (MPa)	Temperature (°C)	Heating rate (°C s^{-1})
Fast	0.5	0.1	100–1200	10–200
Slow	300–7200	0.1	300–600	0.1–1
Microwave	<30	5–20	300–700	0.5–2
Flash	<1	0.1	900–1300	>1000
Vacuum	<1	0.01–0.20	300–700	0.1–1
Hydro	60–120	10–17	350–600	10–300

exposed by microwaves. While processing microwave pyrolysis, the factors, such as the concentration of microwave, initial moisture content, residence time, and flow rate of purge gas, influence the product quality and yield. High rate of heating is normally featured in fast pyrolysis (10–200 °C s^{-1}). During the fast pyrolysis, liquid products are prone to be observed over the formation of biochar. In general, the fast pyrolysis temperature is executed within the range of 500–1200 °C. Usually, the fast pyrolysis is carried out at the rate of heating greater than 1000 °C s^{-1}. Another emerging technique of pyrolysis is vacuum pyrolysis, where the feedstocks are subjected to thermal degradation in the sub-atmospheric pressure with the absence of oxygen using specially designed reactor. In this case, heating rate, pyrolysis temperature, and pressure are set to be in the ranges of 0.1–1 °C s^{-1}, 0.01–0.20 MPa, and 300–700 °C, respectively. Hydro-pyrolysis is carried out in the reactor with hydrogen atmospheric that is maintained at high pressure. In general, the following parameters are maintained during hydro-pyrolysis. Pyrolysis temperature = 350–600 °C, pressure = 10–17 MPa, residence time >60 s, and heating rate = 10–300 °C s^{-1}.

11.4 Applications of Biochar

11.4.1 Biochar as a Nutrient Source

Biochar is rich in carbon sources obtained from pyrolyzing biomass under low oxygen rates and high temperatures for biofuel generation, and like other charcoal, biochar can be used deliberately to apply to the soil for environmental applications. It consists of highly compressed aromatic structures that prevent degeneration in soil and thus can efficiently segregate a part of the applied carbon for decades to era. Further to biochar's promising segregator, recently stabilized atmospheric carbon, its high surface area, porous structure, and affinity for charged particles allow it to interact with the physical and biological constituents of the soil, leading to biodiversity. It can have cascading effects throughout the system. Various recent studies emphasized the advantages of adding biochar to agricultural fields. These advantages contain increased water-holding capacity, enhanced plant growth, reduced crop disease incidence, limited heavy metal bioavailability, reduced NO_2 emission in the soil, and reduced nutrient leaching losses. Raw materials and pyrolysis aspects significantly alter the pH, nutrients, structures, and biochar phenolic content. Various factors, including climate, soil nature, and fertilization conditions, may lead to uncertainty in how biochar interacts with organisms.

11.4.2 Effect of Biochar on Soil Microbial Structure

All changes in soil caused by biochar can alter the composition of microbial biomass and communities in the soil. Figure 11.2 presents absorption of nutrients and hinder the microbial growth on the plant using biochar. The porosity of biochar generates a conducive environment for plant microbes and root growth. As a result, microbial

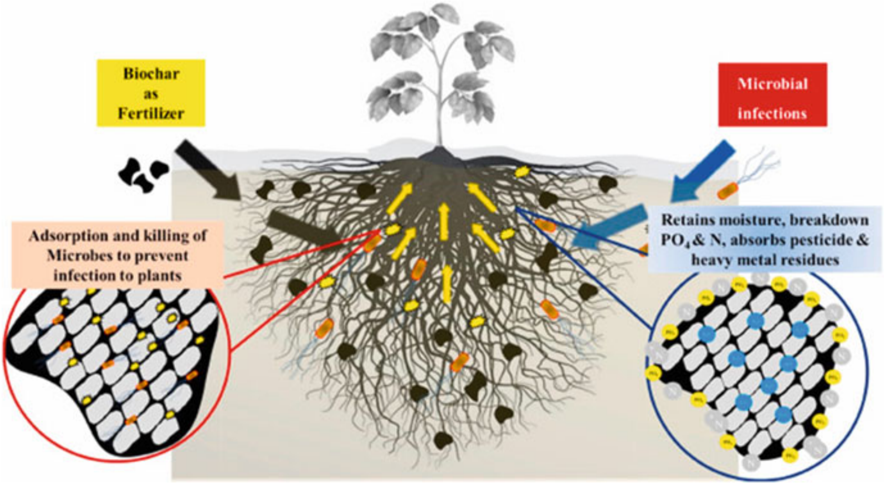

Fig. 11.2 Absorption of nutrients and hinder the microbial growth on the plant using biochar. (*Reused with permission from Elsevier publications*) (Hou et al. 2022)

growth, enzymatic activity, and nutrient cycling are absolutely affected. Furthermore, biochar is composed of macropores, mesopores, and micropores, making it an ideal space for improving various microorganisms such as bacteria and fungi (mycorrhizal, ectomycorrhizal, and arbuscular mycorrhizal). Its porous arrangement provides a supportive environment for microorganisms and further protects them from predators.

11.4.3 Effect of Biochar on Suppressing Plant Diseases

Overall biochar treatment was 86%, 100%, 100%, 96%, and 96% against fungi, oomycetes, viruses, bacteria, and nematodes, respectively, compared to untreated controls. It showed a 50% effective disease control effect. In some cases, an increased incidence of disease was noticed after the use of biochar. Indeed, in bacteria, we observed very high uncertainty between case studies in which biochar had an adverse effect on disease control. A number of studies have shown the efficacy of biochar against the pathogen present in the soil, particularly *Ralstonia solanacearum*. Mushrooms also differed greatly in their responses when it came to disease suppression. In studies on airborne pathogens, the application of biochar derived from various wood was able to control diseases caused by *A. solani* on *S. lycopersicum*, and *B. cinerea* on *Fragaria* × *ananassa*. Biochar from green waste, straw, and shells is effective in preventing *A. solani*, *B. cinerea*, *L. taurica*, *M. oryzae*, *P. corylea,* and *P. mori* (De Tender et al. 2016; Wang et al. 2019). The capability of biochar to suppress soil-borne infectious agent has been exhibited in *Fusarium* sp. *F. oxysporum, F. proliferatum, F. verticillioides, F. solani, F. torulosum, V. dahlia, R. solani, and S. rolfsii.* At last, considerable uncertainty in disease suppressing the efficacy of biochars has also been noted in oomycetes and viruses. Hence, the use of biochar can be potentially accomplished to control microbial plant pathogens (Wang et al. 2019; De Tender et al. 2016). The biochar is known to decreases the severity of plant diseases and promotes plant disease resistance. This is probably by enhancing nutrient retention, changing microbial communities, decreasing soil acidity, and enhancing soil structure. For example, the spreading of *R. solani* on cucumber can be controlled by biochar. Biochar supplements are effective in reducing disease indicators and controlling bacterial wilt. As a result, plant diseases are controlled with the help of biochar supplementation. However, most attempts to use biochar have been in the laboratory for short periods (Chen et al. 2020).

11.4.4 Case Studies on Suppression of Plant Diseases Using Biochar

Li et al. (2022) investigated the application of biochar significantly decreased wilt incidence in flue-cured tobacco, with considerable resistance. The addition of biochar enhanced the composition of the microbial diversity in the soil. Biochar application led to the availability of advantageous microorganisms and decreased *R. solanacearum* populations in the rhizosphere. However, biochar was noticed to have less effect on soil electrical conductivity, with high concentrations (>2%) adversely affecting soil health, plant growth, and dry matter accumulation and has not significantly affected the colonies of *R. solanacearum* in the rhizosphere. Further research focused on improving the control efficacy of biochar against bacterial tobacco wilt by connecting the application of biochar and biochar-enhanced biocontrol agents and analyzing its fundamental biocontrol mechanisms. Gao and Tian (2021) studied the efficiency of biochar in controlling the bacterial wilt caused by *R. solanacearum* on tomatoes and studied the synergetic effect between the biochar-activated modifications in tomato growth, rhizosphere composition, and pathogens. Results exhibited that biochar supplementation reduced disease incidence by 61–78% while improving plant growth. It may be related to changes in the composition of amino and organic acids. Biochar induced an increase in rhizosphere citric acid and lysine and a decrease in salicylic acid, improving the activity of microbes and making the rhizosphere inappropriate for the growth of *R. solanacearum*. Furthermore, nutrients made available by stimulated microbial activity, or supplied by biochar, may improve plant vigor and improve disease resistance in tomatoes. They emphasize that biochars' ability to control tomato bacteria's wilting may be related to changes in the rhizosphere amino and organic acids composition, but in these "biochars" under field conditions, further research is needed to verify the effect.

11.4.5 Mechanism of Biochar on Organic Content in Soil Structure

Chen et al. studied the mechanism and factors affecting biochar's organic content in the soil layer. They observed that because of its large specific surface area, biochar promotes the development of soil accumulates and forms a constant inorganic-organic network by adsorption (Liu et al. 2017); it promotes the soil. The formation of soil organic matter is obtained from plant and animal debris, and organic fertilizers employed in the soil and the decomposition of microbes (Kotroczó et al. 2020). The organic matter composition is complex, ranging from simple chemically structured mono- or polysaccharides to complexly structured humus, from plant debris of pectin, hemicellulose, and cellulose to the integration of plant residues, including root exudates and mineral particles. It extends to decomposition products such as mycelia that have been processed and aggregated from the ground. Compared to short-term applications, long-term biochar applications have been shown to expand the structure of soil biochar particles and increase their volume to store cations and organic matter.

11.4.6 Influencing Parameters of Biochar on Organic Content in Soil Structure

Plaza et al. (2016) experimented with the effect of biochar on the soil layer. Results exhibited that biochar can enhance the organic matter composition in each layer of the soil. Analysis has found that stable factors driven by biochar contribute instantaneously to soil organic matter (Plaza et al. 2016), whereas labile biochar components, in the form of soluble organic matter, contribute to soil carbon storage. The biochar with a large surface area and pore structure added to the soil can improve the soil's ability to adsorb and hold organic matter. Shortening soil carbon loss has been suggested (Suliman et al. 2017). Furthermore, surface oxidation occurs after biochar is employed in the soil, imparting a negative surface charge to the organic matter-mineral complex, thus improving the formation of soil agglomerates. Remediation of anthropogenic sedimentation soils using appropriate amounts of biochar is, therefore, one of the promising results for enhancing water and fertility retention and extending the service life of soils in semiarid regions. However, the effect of biochar on decomposition to organic matter needs further investigation. Due to the scarcity of water resources globally, water-saving irrigation must be implemented. Use biochar to enhance soil, study the effects of various application amounts on soil structure, and clarify its comprehensive impact mechanisms to improve soil structure and popularize biochar application.

Applying biochar is a useful method for improving soil cohesion in semiarid areas. It could be a promising method for enhancing soil organic matter and stability. Relationships between key indicators with quantitative descriptions are suitable for accurately formulating water conservation management. Simulation relationships provide data support for biochar's financial and effective use and a theoretical basis for water-saving irrigation management in agriculture (Cen et al. 2021).

11.4.7 Effect of Biochar on Soil Enzymes

Biochar is generally regarded as a substance that resembles charcoal in its appearance, but it is made from constituents such as burnt agricultural and forest wastes. They are converted into this kind of biomass by thermochemical methods under limited oxygen availability. Soil is generally subclassified based on its color, texture, and fertility. One such type is the red soil, primarily found in regions like China, South America, and Southeast Asia and has extensive use in agriculture in the respective areas. However, a major problem associated with red soils is that they are highly susceptible to erosion and weathering. Thus, it is necessary to uphold the aggregates in the red soil to prevent soil weathering and erosion. With the help of research and studies, it is found that an increase in the carbon content in the soil helps in the prevention of soil erosion and helps in the formation of soil aggregates. The microorganisms present in the soil tend to decompose the organic matter with the help of enzymes and replenish the quality of the soil. Thus, biochar, a stable organic matter created at thermal conditions between 350 and 600 °C, has shown an increase in the enzymatic activity of the soil microbes and replenishes the soil quality as well.

The researches and studies support an increase in the enzymatic activity of the microorganisms present in the soil due to increased biomass when the biochar is introduced into the soil environment. Biochar also plays an important role in improving the soil's macronutrients, especially nitrogen and potassium, and predominantly helps maintain soil fertility. Biochar generally increases the soil porosity when introduced, thus making it favorable for the microorganisms by providing shelter and thus increasing the microbial population, increasing the total enzyme production and enzyme activity. The activity of any enzyme depends on the optimal conditions for that particular enzyme, biomass availability, the population of the microorganisms producing the enzyme, and the physical and chemical conditions of the soil. Since biochar directly correlates with the improvement in the soil's physical and chemical characteristics, it indirectly influences and increases the enzymatic activity of enzymes in the soil (Mierzwa-Hersztek et al. 2016). Nitrogen, a macronutrient, is extremely important for yield and soil productivity when growing crops like soybeans. As a result, biochar can be considered the most promising ingredient for producing soybeans and other crops. The property of the soil to retain water and the effectiveness of the enzymes produced by soil-borne microorganisms to maintain soil quality are two essential characteristics required for the production of soybeans. In order to enhance the survival rate of the *Rhizobium* and the rate of soybean nodulation, biochar has also been investigated as a *Rhizobium* inoculant carrier. Biochar can offer a habitat for bacteria because of its porous structure, which has a large interior surface area and a high propensity to cling to soluble organic materials (Ma et al. 2019).

The soil enzymes are also significantly stabilized by biochar. The soil microbial density rises due to its porosity, which draws in and offers a home for soil-borne microorganisms. The enzymatic activity of the microorganisms has increased six to eight times because there is a larger context of biomass for the bacteria and appropriate circumstances for the enzymes, and they maintain the soil environment and safeguard the extracellular enzymes needed for the quick depolymerization processes of the soil organic matter; the primary defense comprises preventing the extracellular enzymes from experiencing environmental stress, which increases their enzymatic activity and boosts production and fertility as well (Pandey et al. 2022). Thus, on the whole, biochar is regarded as one of the potential additives for the soil to increase fertility and primarily in increasing the activity of the extracellular enzymes produced by the soil microorganisms.

11.4.8 Effect of Biochar on Microbial Diversity

Biochar is a material that is rich in carbon and has a rich surface functional group, specific surface area, high porosity, and strong adsorption, which is obtained by pyrolysis of crop straw, livestock manure, wood materials, and other organic material at low oxygen environment and low-temperature range from 300 to 700 °C (Wang et al. 2022a). With the help of biochar, certain microorganisms are also protected from predation and increase microbial diversity. By changing the soil properties, biochar indirectly impacts soil microbial diversity. It increases cation exchange capacity, soil pH, porosity, and soil aggregation (Song et al. 2020). The biochar effect on microbial, fungal, and bacterial diversity was determined by the pyrolysis temperature and the feedstock type used for the biochar production. Its effect also depends upon soil texture and experimental conditions. The effect of biochar on bacteria was also significantly affected by soil pH (Wang et al. 2022b).

The effects of biochar on soil bacterial diversity were also significantly affected by soil pH, with significant increases with pH 6.5. The particle size of the biochar also affects microbial diversity. The biochar with a particle size of 2 mm significantly increases the diversity of bacteria, whereas the biochar with a particle size of 1 mm significantly decreases the fungal diversity (Yin et al. 2021). The application of manure biochar increases total microbial and bacterial diversity. In contrast, the sludge biochar will increase the total microbial and fungal diversity, but the straw and residue biochar will increase only the bacterial diversity. The amount of microbial, bacterial, and fungal diversity also depends upon the biochar pyrolyzed at a different temperature. Adding biochar pyrolyzed at 700 °C increases total microbial and bacterial diversity, whereas biochar pyrolyzed at 300 °C increases fungal diversity (Wang et al. 2022b) And also, in terms of pH, bacteria will sustain in high pH compared to fungi, so the bacterial diversity was more in high pH. In bulk soil, the addition of biochar will increase the fungal diversity and decrease the bacterial diversity, which could be related to the changes in chemical properties as soil properties will have a greater impact on bacterial than fungal diversity. In acidic and sandy soils with low organic carbon content, adding biochar will increase the total microbial diversity (Li et al. 2020a, b). Low rate and long-term biochar addition increase microbial diversity. Biochar would also alter soil physicochemical properties, increasing available phosphorus, total nitrogen, nitrate nitrogen, ammonium nitrogen, and water content.

The addition of biochar significantly improved the clayey raw soil's lack of fertility and low soil microbial diversity. Biochar application increased bacterial and fungal biomass and diversity in acidic soils. Acid soils also showed the greatest increases in total microbial biomass. Biochar application is a cleaner production method recommended to improve soil health and reduce environmental footprints. Biochar activity improved soil carbon dynamics while decreasing GHG emissions from CI paddy fields. Applying biochar to acid soils neutralizes soil acidity, increasing nutrient availability, which contributes to increases in microbial biomass and diversity. High biochar application rates may affect microbial diversity because they drastically disrupt the microenvironment required for microbial growth.

11.5 Future Directions and Prospects

A growing number of studies in the field of environmental science exploit the applications and potential of biochar, particularly in how it might manage the environment and reduce carbon dioxide emissions. Biochar is considered an excellent material for mitigating various kinds of environment-related issues. While its effects on soil remediation and greenhouse gas emission reduction are very well studied, the unlimited potential of biochar still needs to be explored. Recently, the pollution alleviation effects of the biochar obtained from various agricultural wastes have been widely studied. The exploitation of biochar for its ability to adsorb various environmental pollutants ranges from antibiotics to heavy metals. For instance, Varadharajan et al. (2022) used biochar derived from cotton dust to adsorb antibiotic tetracycline from wastewater. The presence of antibiotics in various environmental sources is linked to the development of antibiotic resistance in pathogenic microorganisms. Also, numerous studies have confirmed the phytotoxic and aquatoxic nature of various antibiotics (Benassi-Borba et al. 2021). Using cotton dust-derived biochar to treat antibiotic-contaminated wastewater resulted in the effective removal of 97% of tetracycline. In contrast, the biochar derived from agricultural discards showed tetracycline removal of up to 9.45 mg g^{-1}.

The antibiotic adsorption capacity of biochar is remarkably high, and it depends mostly on the specific surface area of the biochar. Additionally, surface treatments with activators enhance the antibiotic adsorption capacity of the biochar. For example, Zhang et al. (2022) performed the chemical activation of sesame straw-derived biochar using KOH and $Ca(OH)_2$ to enhance the material's pore size. The biochar had a very high surface area of 935 m^2 g^{-1} and displayed high adsorption capacity toward antibiotics such as ciprofloxacin, norfloxacin, and enrofloxacin. Apart from adsorbing antibiotics from aqueous solutions, biochars are shown to protect plants directly from the effects of antibiotics by absorbing antibiotics from the soil. Vu and Ahmed (2022) devised a study utilizing the antibiotic adsorption property of rusk husk-derived biochar to prove that phytotoxicity ameliorates the effect of biochar. In their study, the soil contaminated with antibiotics such as tetracycline and sulfamethazine did not support the development of seedlings of various plants. However, seed germination rates improved after treating antibiotic-contaminated soil with biochar, and the phytotoxic effects associated with antibiotics were reduced.

Another important area in the environment where the most emphasis is needed is the mitigation of pesticide residues. Even though pesticides are essential for better crop yield, their effect on soil microbial diversity and subsequent surface and groundwater contamination make them an environmental pollutant. The serious threat posed by pesticide-related pollutants resulted in the creation of several novel adsorbents that can effectively remove residual pesticides from various environments. One of the most commonly researched adsorbents is biochar. The organic compound adsorption properties of biochar are excellent; hence, recent research is focused on using biochar for the remediation of sites contaminated with pesticide residues. The use of wood-derived biochar to remove pesticides such as atrazine, endosulfan, and chlorothalonil from drinking water was reported by Khan et al. (2022).

Similarly, the removal of ten different pesticides from water using corn cob-derived biochar was described by Alsherbeny et al. (2022). In addition, the removal of organophosphate pesticides using potato peel-derived biochar was stated by Singh et al. (2022). Numerous reports on pesticide-adsorbing biochars prove that biochars can be a sustainable adsorbent material to treat pesticide residues from contaminated sites. While reports on in vitro treatment are available, only a few in situ treatments of the contaminated site with biochars are available. Hence, future studies relevant to the in situ treatment of organic pollutants using biochar can be expected.

Using biochar to treat contaminated sites is not only restricted to organic pollutants. Inorganic pollutants such as heavy metals are commonly observed in almost all environments. Hence, adsorbent materials, including biochar, are widely explored in the current research for environmental remediation from heavy metal toxicants. A study by Ammen and Al-homaiden demonstrated the application of wheat straw-derived biochar to remove various heavy metals from sewage sludge. Their study showed a marked decrease in heavy metals such as cadmium, chromium, copper, and lead when sewage sludge is treated with 4% biochar.

In the current scenario, biochars with tunable properties are used for several environmental applications. The tunable properties include adding or removing functional groups, loading or doping various inorganic elements, changing pore size, and induction of magnetic behavior. A study by Yin et al. (2022) reported the production of corn cob-derived biochar with a tunable sulfur-functional group for the heavy metal adsorption process. Likewise, Qi et al. (2022) have demonstrated the self-doping of magnesium oxide-loaded nitrogen and phosphorus onto the biochar obtained from the fish scale for the adsorption of heavy metals like copper, cadmium, and lead. All these latest studies indicate that the properties of biochar can be modified to the extent that they can be applied to solve environmental problems.

11.6 Summary and Outlook

Biochar is a proven candidate for managing contaminants because of its excellent environmental remediating proficiency. It is proven that the futuristic biochar applications critically depend on the assessment of the steps and existing gaps in commercialization of large-scale production. In order to produce a high-valued biochar, various researches still have been carried out. In this chapter a state-of-art for biochar production from different agro-residual has been reviewed. Consequently, various agro-residues, contemporary approaches for biochar production, influences of soil amendments, and applications towards the environmental bonification have been summarized.

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Valorization of Sugarcane Bagasse Fly Ash Into a Low-Cost Adsorbent Material for Removal of Heavy Metals: A Review

12

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Abstract

Management of agricultural waste is the need of the hour as disposal of these wastes poses a serious environmental problem. Rapid development in the agriculture sector is generating large quantities of agricultural waste, which require immediate attention as their disposal consumes a lot of useful land area and also threatens the environment. Sugarcane bagasse is one such material that evolved during the production of sugar, when consumed as a biomass fuel, it results in the creation of another solid waste known as bagasse fly ash (BFA). A significant portion of BFA contains aluminous and siliceous materials along with a small quantity of carbon. This high silica and alumina content present in BFA can serve as a raw material for the synthesis of zeolitic materials. Further, these BFA-derived zeolitic materials can serve as low-cost adsorbents in the decontamination of wastewater infested with heavy metals. The current review aims to provide a potential solution for the valorization of BFA by reviewing the best possible areas to expand the use of BFA considering environmental concerns.

Keywords

Adsorption · Bagasse · Fly ash · Heavy metal · Zeolite

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12.1 Introduction

Sugarcane is one of the financially viable cash crops all around the world due to the never-ending demand for sugar. Sugar production is a complex process that involves several stages of treatment and various raw materials throughout the production generating various waste materials at each stage (Khandelwal et al. 2022).

12.1.1 Sugarcane Bagasse Fly Ash

Sugar mills contribute to environmental pollution by producing wastewater, emissions, and solid waste. The quantities of sludge produced from the plant when disposed to the stream affect the aquatic life by causing severe foul conditions. The foul emissions from the sugar industry cause an obnoxious smell around the plant. However, the solid residues liberated during juice extraction known as bagasse are one such major solid waste generated from the sugarcane industry. The solid residue material is what is left of cane fibers squeezed out of sugarcane juice. Approximately 33% of cane sent for crushing is returned as bagasse solid residue (Anastopoulos et al. 2017). Bagasse is a rich fibrous material with high biochemical oxygen demand produced by the sugarcane industry at an alarming rate. The improper handling and disposal of this bagasse waste can cause severe environmental concerns. Approximately 3 tons of wet bagasse is produced by sugar factories for every 10 tons of sugarcane crushed (Akarsh et al. 2022). The bagasse produced is rich fibrous material with a calorific value of 1920 kcal kg^{-1}, which can serve as a fuel fed to boilers for the steam-based generation of electricity. During this process, the burning of bagasse waste generates fly ash collected from electrostatic precipitators. This Bagasse fly ash (BFA) is a very light material with the possibility of toxic metals and can cause secondary air pollution when left unaddressed. BFA contains a large amount of unburnt carbon and can have various adverse impacts on humans, plants, and animals through water, air, and soil pollution (Patel 2020; Gupta and Sharma 2003). Similarly, press mud and molasses are some other important wastes generated by from the sugar industry. Press mud cake is the precipitate in the form of sludge slurry left after filtration. It is a residue of the sugarcane juice filtration process comprising all non-sucrose impurities as well as carbonates, phosphates, and sulfates. This nutrient-rich press mud can be used as a fertilizer. The by-product left after the process of crystallization of sugar in the sugarcane industry is known as molasses (Anastopoulos et al. 2017). Molasses is a black viscous liquor that contains 30–50% of sugar by weight and other organic and inorganic compounds. The trace compositions of dietary metals present in molasses make it a nutritional animal feed; however, the production of ethyl alcohol has proven to be a better alternative. The molasses is sterilized, diluted, and fed to the fermenter where the sugars are broken down into simple alcohols like ethyl alcohol in anoxic conditions by the alcoholic fermentation of molasses by microorganisms (Lin and Tanaka 2006).

The by-products of the sugar industry create a huge impact on the environment. The sugar industry prominently contributes to environmental pollution. It generates wastewater, emissions, and solid waste. The large quantities of plant matter and sludge get washed away from the mills and get decomposed in the lakes and rivers, and aquatic animals get affected as they deplete the available oxygen. Apart from this, they produce flue gases, soot, ash, ammonia, and other substances that are released into the atmosphere. If this continues, it will generate a huge burden on the environment. This turns out to be a serious issue if these by-products are not managed well. Exploring the potential of these by-products will assist in studying their application in various fields such that it reduces the burden on the environment. If these products from the sugar industry can be used as raw materials to turn them into viable products, it can significantly reduce the environmental pollution loads, and the waste generated from the sugar industry will be resourcefully managed. Hence, wastes generated from various stages of sugar production are duly considered and converted into value-added products to avoid any further contamination. This can avoid a huge burden on the environment and leads to a path of sustainability (Anastopoulos et al. 2017). Figure 12.1 depicts the schematic representation of wastes generated during sugar production and their applications.

On the other hand, industrial expansion has resulted in the growth of the country's economy. But the rapid industrialization has also led to the contamination of wastewater. Heavy metal contamination is a serious issue that is a repercussion of industrial growth. This has to be dealt with as this is becoming a serious environmental issue. As the effluent from various industries like a tannery, fertilizer industry, and the textile industry gets discharged into the streams, it gets contaminated and poses a threat to the environment. These discharges would have the presence of heavy metals that are toxic in nature and is necessary to remediate them before they enter the river or ocean. The heavy metals have the potential to damage aquatic life once it enters the stream (Kumar et al. 2019). Therefore, an effective way to remove these heavy metals from wastewater has to be found so that safe discharge of wastewater can be carried out. Various ways to remove heavy metals from wastewater exist like chemical precipitation, ion exchange methods, and biological methods. Due to the high cost of operation and problems in sludge generated after the treatment methods, they are being not in use much. The use of activated carbon in adsorbing the heavy metals from wastewater is another way of removing toxic metals, but the use is declining due to the high cost. Hence, it is important to switch to a method that is cost-effective as well as removes heavy metals at higher efficiency (Oliveira et al. 2019).

The use of waste-derived adsorbents has to come into play, which effectively removes heavy metals and is cost-effective. Researches are ongoing to make use of various industrial waste to explore their potential in turning them into an adsorbent. One such application is being explored in the agricultural industry to make use of agro-waste and turn them into a viable product. India is one of the countries that produces sugarcane, and the waste associated with them is much higher. The by-product of the sugar refining industry is BFA, which creates trouble in the disposal. The chemical composition of BFA is promising to be a viable adsorbent; however, it is limited by its availability of unburnt carbon. However, the silica and alumina-rich BFA can act as a precursor material for zeolites, which possess larger

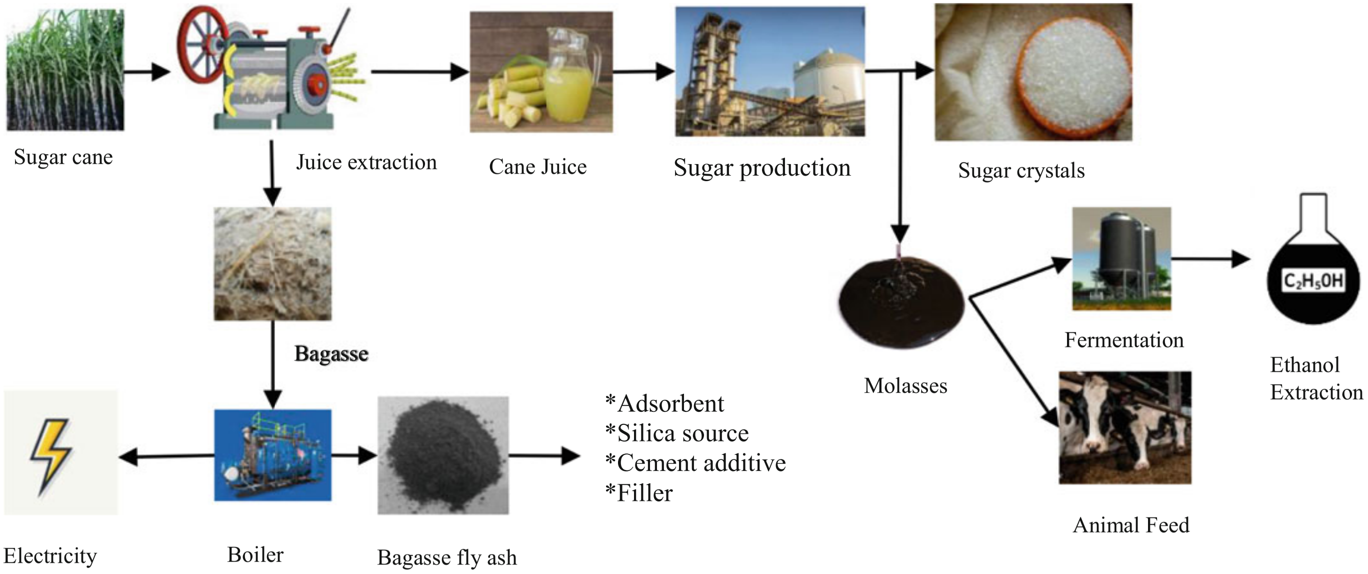

Fig. 12.1 Schematic representation of cane sugar manufacture and possible applications of by-products recovered

surface area and better cation exchange capacity (CEC) than their original materials (Anastopoulos et al. 2017).

The current manuscript aims at depicting the possible applications of BFA in various fields. Furthermore, it aims at apprising BFA-synthesized zeolite from various synthesis techniques and their subsequent application in the removal of heavy metals from contaminated wastewater.

12.1.2 Composition of BFA

The finest particle size of BFA ranging from 0.5 to 300 microns with its lightweight character tends to suspends in the air creating air pollution and problems related to respiration when left unattended. The BFA also contains heavy metal traces that can create groundwater contamination. These issues should be dealt with rather than disposing of the BFA in landfill areas and adding to problems. For the same, its properties have to be studied and thoroughly examined for understanding its applications. For exploring its application in various fields, it is important to study its physical and chemical properties. BFA mainly consists of calcareous materials, which comprise major proportions of silica and alumina and calcium oxide and magnesium in minor parts. It also comprises metal oxides such as iron oxides, magnesium oxide, titanium oxide, and potassium oxide. After various characterization techniques, it is found that it has been found that BFA has a very high quantity of amorphous calcareous materials, unburnt carbon, surface area, and pore size, and thus according to its properties, it can be utilized in suitable fields (Patel 2020). The specific gravity of BFA has been reported by many researchers, and the specific gravity relates weight-to-volume relation of the BFA, which aids in its application as a pozzolanic additive in various fields. The specific gravity of BFA reported by the researchers ranges from a minimum of 1.13 to a maximum of 2.69 due to the variations in the sources of sugarcane procured (Tripathy and Acharya 2022). Table 12.1 illustrates the chemical compositions of BFA produced around the world.

Table 12.1 The chemical compositions of various BFA available around the world

Chemical composition	SiO_2	Al_2O_3	Na_2O	CaO	MgO	Fe_2O3	K_2O	LOI
Oluyinka et al. (2020)	83.14	1.53	–	2.6	1.6	6.06	4.23	0.84
Purnomo (2013)	49.98	2.2	–	2.78	1.65	1.22	3.97	–
Shah et al. (2013)	70.92	2.52	–	5.06	–	–	4.84	–
Shah et al. (2011)	45.33	12.04	0.4	4.59	5.26	5.86	1.12	–
Praipipat et al. (2023)	77.2	1.97	–	26.47	2.98	–	4.09	–
de Franca Araujo Filho et al. (2021)	49.16	17.39	–	5.4	9.8	1.14	4.64	4.89
Moisés et al. (2013)	86.2	2.8	–	1.5	–	2.9	2.4	0.7
Tobarameekul et al. (2022)	70.81	17.4	–	–	–	4.34	–	–
Jangkorn et al. (2022)	72.8	9.16	0	3.34	1.47	5.05	3.84	4.34

12.1.3 Applications of BFA

BFA is a silica-rich material with little amounts of unburnt carbon, which suggest its applicability in fields of adsorption. Similarly, the silica-rich material can be imparted with pozzolanic properties and can be used in the cement industry as well as a value-added material in various construction practices.

12.1.3.1 Construction Industry

The cement and construction industry consume a lot of raw materials, majorly calcareous and agricultural materials. These materials are a part of the earth's top layer, which is fertile and meant for the survival of flora and fauna. This scraping of the earth for raw materials can be avoided by implementing the usage of wastes generated in various industries. BFA is one such waste generated, which is rich in silica, and alumina content, which matches the requirement of raw materials used in the cement and construction industry. Various investigations carried out on the usage of BFA using California bearing ratio, unconfined compressive test, and triaxial test reported that BFA has properties similar to cementitious material and can be used as an additive or resource in the construction industry (Patel 2020). BFA blended in concrete improved the consistency of concrete twofold and on other hand increased the water demand due to its hygroscopic nature. Furthermore, the expansion of the mortar bar was observed to be limited by 46% when 40% of cement is replaced with BFA (Kazmi et al. 2017). The addition of any cementitious materials like BFA will influence the properties of concrete like water demand, hydration, setting time, etc., and the addition of BFA in excess can increase the water demand due to an increase in surface area and decrease the setting times as the replacement of cement using BFA can reduce the C_3A content in concrete mixture delaying the setting times of concrete (Ahmad et al. 2020).

The application of BFA as a stabilization material to expansive soils has proven to be effective; an effective 6% replacement has improved the California bearing ratio by 41.52% and compressive strength by 43.58% (Kharade et al. 2014). A similar study carried out on improving black cotton soil reported a 27.89% reduction in the plasticity index and an improvement in compressive strength when 8% of soil is replaced with BFA (Arya et al. 2022). A study carried out on improving the characteristics of clay using a blend of BFA and ordinary Portland cement revealed the addition of 20% of BFA can enhance the strength of clay as much as compared to the addition of ordinary Portland cement (Jamsawang et al. 2017). Stone mastic asphalt is a gap-graded asphalt with a higher amount of asphalt in it. Usage of conventional fillers can consume too many argillaceous materials, which may lead to environmental issues. The investigation carried out by replacement with BFA revealed improvement in characteristics of asphalt mix in terms of stiffness and flow characteristics and also improved the moisture resistance by 7.5% (Akarsh et al. 2022). The performance of BFA an additive has been carried out by omitting the unburnt particles and coarse particles by sieving. The sieved sample was mixed with hydrated lime to create a lime binder, which reported a 50% enhancement in the pozzolanic activity compared to that of the original BFA. Furthermore, there was a

30% increment in the compressive strength of the sugarcane BFA–Lime binder (Potiron et al. 2022).

Replacement of fly ash and slag-blended concrete with bagasse ash blended with concrete has shown better results in terms of resistance against chloride and water permeability. In comparison with the control sample, a 32% reduction in chlorine control index value has been recorded for 25% replaced BFA concrete in 28 days (Bahurudeen et al. 2015). Similar investigations have reported the production of a high-strength concrete using BFA and lime powers, which not only met the minimum required strength of 55MPa but also significantly reduced the chloride ion passing charge (Klathae et al. 2021). Bagasse was used as a substitute for fly ash and slag in blended cement at various replacement levels ranging from 20%, 30%, and 50%, and the characteristics and performance were studied and compared with fly ash and slag blended cement. There were a few contrary effects such as delayed initial set, workability reduction, and increased consistency in the case of bagasse-blended concrete. The strength gain of bagasse-blended concrete was better than the fly ash and slag blended concrete, and a significant enhancement was also found towards chloride and water permeability (Minnu et al. 2021).

Conducting a series of an experiment comparing normal bricks and bricks manufactured with BFA showed that the latter had better compressive strength. However, an acceptable substitution of 10% BFA has proven to be effective, beyond which the properties of bricks have been compromised (Faria and Holanda 2013). A similar investigation revealed 10% is an optimum replacement for clay in ceramic tile production, which limited the strength of tiles (Faria and Holanda 2013). However, an investigation carried out by incorporating 10% of lime along with 10% of BFA revealed better-performing bricks with a reduction in the required energy for production (Alavéz-Ramírez et al. 2012).

Turning the by-product of the sugar industry into a viable product will minimize the issues related to the disposal of waste. Conventional cement is being replaced with blended cement using industrial by-products like BFA, fly ash, and slag practiced as a step toward sustainability. The pozzolanic activity of BFA makes it a viable resource material in constriction practices.

12.1.3.2 BFA as an Adsorbent

The adsorption phenomenon is majorly dependent on two of the materials involved in the reaction, that is, adsorbent and adsorbate. The adsorbent is the material that is adsorbed on the surface and is available in bulk, and the adsorbate is the material that is being adsorbed on the surface of the adsorbent material. The adsorption phenomenon is well connected with the surface of the adsorbent. To increase the adsorption rate, the adsorption surface has to be porous, and it will eventually increase the percentage of the removal of targeted contaminants or adsorbate. Surface area characteristics using BET and pore parameters aid in better understanding the adsorption phenomenon (Patel 2020). Adsorption has proven to be the most viable option in the treatment of various contaminants from waste streams such as dyes, metals, phenols, insecticides, herbicides, pharmaceutical products, and chemicals contributing to COD, BOD, and color. BFA is one such material with a small portion of unburnt carbon and mineral oxide compositions distributed as a very fine particle with a large surface area and more pores for receiving various contaminates (Batra et al. 2008). These characteristics of BFA have encouraged the scientific community to explore the properties of BFA further as a potential cost-effective adsorbent.

Dyes are among the common industrial effluents, which create toxic environments. These materials are used in textile industries for aesthetically pleasing fabric. The dyes are mostly organic with a high COD load and a high color, which create an obnoxious environment when released into the environment. However, complete treatment of dyes was considered an ineffective method, and adsorption became a feasible option. Adsorption became a viable option due to its effectiveness and regeneration capabilities. The search for potential low-cost adsorbents explored various industrial by-products and ashes from electrostatic precipitators that served the purpose due to their active pores and enlarged surface areas. BFA is one such material eluted from the sugar industry used as an adsorbate. An investigation carried out using rhodamine-B and methylene blue adsorption using BFA implied a maximum removal concentration of 14.3 and 0.202×10^3 moles g^{-1} observed revealing the effectiveness of BFA as an adsorbate compared to commercially available adsorbents (Gupta et al. 2000). A similar investigation performed using brilliant green dye revealed that BFA is an effective adsorbent for the efficient dye removal, particularly at a low initial concentration and acidic pH levels of approximately 3 with an optimal adsorbent dosage of 3 g L^{-1} (Mane et al. 2007). Adsorption studies on acid orange -II dye using BFA revealed its effectiveness as an adsorbent; by varying the adsorbent column temperature, length, initial concentration, and flow rate, complete adsorption was achieved at 45 °C, 45 cm, 100 mg L^{-1}, and 1 L h^{-1} (Kanawade and Gaikwad 2011). A series of adsorbents prepared using a mixture of bagasse, BFA, titanium dioxide, magnesium oxide, and fly ash revealed that the addition of metal oxides improved the adsorption and the addition of magnesium oxide improved the adsorption of rhodamine blue by 93.78% for a dye concentration of 50 mg L^{-1} and dosage of 2 g/100 mL. A pseudo-second-order kinetics model described adsorption as chemisorption (Praipipat et al. 2023).

A study toward inexpensive and effective adsorbent leads to the application of BFA as an adsorbent for the removal of lead and chromium. The removal efficiency of lead and chromium reached 95–96% by column experimentation studies. The maximum adsorbent capacity of BFA reached 35.0 and 25.0 mg g^{-1} for lead and chromium in column studies compared to 30.0 and 20.0 mg g^{-1} in batch studies. The variation is attributed to the continuous availability of high-concentration gradients available in column studies (Gupta and Ali 2004). A similar investigation carried out on the adsorption of cadmium, nickel, and zinc using BFA revealed the spontaneous adsorption of metal ions onto the adsorbent. The temperature has a pronounced effect on the adsorption, and the endothermic process improved the metal ion mobility improving the adsorption capacity of BFA. However, the adsorption followed an increase in their atomic weights and their ionic radii, that is, Ni (II) >Zn (II)>Cd (II) (Srivastava et al. 2007). Further, the limited availability of unburnt carbon has been a setback for BFA application in fields of adsorption. However, the similarity of composition to the volcanic ashes, which are rich in silica and alumina led the scientific community toward the modification of BFA into zeolites. The unburnt carbon along with BFA modified in zeolite acts as a strong adsorbent for metal ions. The modification process and adsorption characteristics of zeolites derived from BFA are explained in the following parts of the manuscript.

12.1.3.3 Other Applications

Sugar industry wastes are a promising resource for utilizing in remediating wastewater and thus have the potential to reduce the environmental burden (Anastopoulos et al. 2017). Various researchers working on exploring the applications of BFA. Catalytic operations involve the use of metals, metal oxides, and a mixture of metal oxides. The inexpensive BFA contains metal oxides like alumina, silica, and other metal oxides along with unburnt carbon, which acts as a housing unit for any metals that serve as a catalyst. A study was conducted based on loading Fe meats onto an unburnt portion of BFA used in the oxidation of n-Butanol. The sieved unburnt carbon content was calcined and treated with phosphoric acid and then loaded with iron using iron nitrate. There was no complete transformation of n-Butanol; however, the potential of catalytic support of waste-derived materials proved to be more suitable for catalysis than the iron-loaded activated carbon materials used as catalysts (Pande et al. 2012). An investigation carried out on the application of calcined BFA as a catalyst in the production of jatropha seed oil methyl esters revealed an excellent conversion of 92.84 wt. % of biodiesel recorded for a 10% weight ratio of catalyst. This study revealed that abundant, renewable, and highly economically viable BFA can be developed into an excellent catalyst for biodiesel production (Basumatary et al. 2021). Similarly, BFA has proven to be a viable catalyst in various applications like dehydration of methanol to diethyl ether, and the high thermal stability, heterogeneous nature, abundance, and economic viability characteristics of BFA make it a promising catalyst (Patel 2020).

12.2 Synthesis of Zeolite from Bagasse Fly Ash

Agricultural wastes pose a serious threat to human health through environmental pollution, and their improper handling may lead to a huge economic loss. A sustainable approach to the management of agricultural waste would be to use them as resource materials. This would lead to proper waste management, recovery of energy, and saving of precious resources, which ultimately benefits the environment. BFA in its natural form can be utilized in various fields as discussed by different researchers; however, to maximize its benefits it is modified and converted into zeolites for further application in the decontamination of toxic metals and organic materials and as a catalyst. The similarity of the composition of BFA to pre-cursor materials of zeolites led the scientific community to carry out investigations on the conversion of BFA into zeolites. The converted zeolite possesses a high CEC value and a larger surface area much more suitable for the capture of cations making it a viable compound for the capture of heavy metals from wastewater.

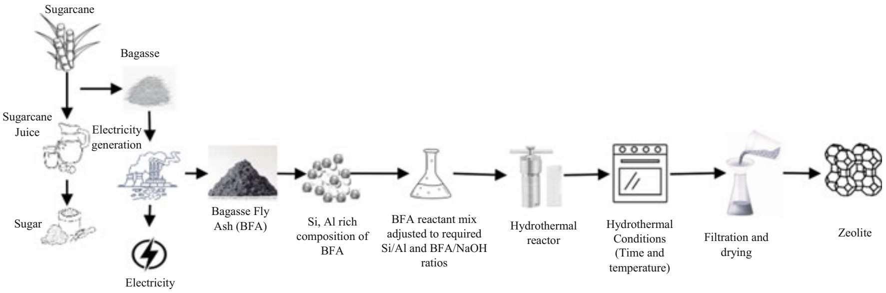

Fig. 12.2 Zeolite synthesis from BFA using hydrothermal synthesis method

Zeolites are aluminosilicates with a three-dimensional frame of work of individually arranged tetrahedrons of $[SiO_4]^{4-}$ and $[Al_2O_3]^{5-}$ interconnected by oxygen atoms. The charge deficit on individual alumina tetrahedrons is responsible for the creation of void spaces of charge deficits, which lures cations. The key steps behind the synthesis of zeolite from BFA involve the dissolution of reactants under alkali hydrothermal conditions, nucleation in the reactant mixture, and crystallization of zeolite (Belviso 2018). Figure 12.2 depicts the step-by-step procedure involved in the synthesis of zeolite from BFA using conventional hydrothermal synthesis techniques.

The ash activation is activated by varying the alkali agent, temperature, and reaction time. NaOH is reported to give the most conversion efficiency; hence, it is chosen as the alkali activator. Temperature and NaOH concentration are two important parameters that govern alkali activation. As the chemical characterization suggests that there is very less amount of aluminum that is readily dissolvable, further dissolutions require higher energies and times suggesting the external source of alumina for quick and effective synthesis. BFA was modified into zeolite using hydrothermal synthesis using 3 mol L^{-1} NaOH with a liquid/solid ratio of 10:1 for 72 h at 373 ± 5 K. Similarly, BFA mixed with NaOH at NaOH/BFA ratio of 1.2 w/w fused for 1.5 h at 823 ± 10 K and then subjected to hydrothermal synthesis 363 K for 6 h upon the addition of 128 mL of DI water. The resultant zeolitic materials zeolite-P and analcime were washed and dried overnight. The fusion step introduced improved the formation of excess aluminosilicate salts, thereby improving the zeolite characteristics like surface area and pore parameters (Shah et al. 2013). A similar synthesis method was carried out using NaOH as a mineralizing agent by hydrothermal treatment after the calcination of procured sugarcane bagasse. The characterization of the obtained result showed that the major parameters affecting the zeolitic materials are temperature and calcination time, which subsequently affects the ion exchange capacity. At 800 °C for about 8 h, calcination was carried out to confirm the removal of all carbons from the source to optimize the ion exchange capacity. Al isopropoxide was added to the synthesis medium to enhance the ion exchange capacity. The fusion-assisted synthesis was carried out using BFA at 600 °C for 8 h, followed by a hydrothermal synthesis step. The resultant zeolite is hydrothermally treated with and without an additional external source of alumina.

The charge deficiency on zeolitic materials is dependent on alumina tetrahedron; hence, the addition of excess alumina resulted in improving the CEC to 142 mg g^{-1} (Oliveira et al. 2019). A composite carbon zeolite is synthesized by segregating the BFA for activated carbon preparation and extraction of silica from the fine portion of BFA. These materials are added during the zeolitization step to form the composite material. This blend retains the carbon qualities along with the newly formed zeolite, making it the best viable adsorbent (Purnomo 2013). Table 12.2 provides information about zeolite synthesis parameters along with the zeolite product and subsequent applications.

The sugarcane bagasse waste, which is quartz abundant, can be used as a silicon source, which can significantly reduce the accumulation of waste. Utilization of BFA as a silicon source can be achieved by the means of alkali fusion extraction method wherein the quartz particles can dissolve and silicon can be used as raw material for synthesizing silica-based materials such as zeolite, which have the potential to be used as an adsorbent. The experimental procedure followed for the synthesis of zeolite followed was collecting the sugarcane BFA from the sugarcane industry and keeping it in a horizontal furnace at 600 °C, and it was kept for 4 h. For zeolite synthesis bagasse fly, ash was mixed homogeneously with NaOH in a ratio of 1.5. The mixture was then heated in a nickel crucible in an air atmosphere of 500 °C for about 40 min. In 1 L of distilled water, the resultant fused mixture was dissolved. Immediately into the silicate solution, an amount of 1.0 L of sodium aluminate solution 0.48 mol L^{-1} (i.e., 39 g sodium aluminate in 1.0 l of distilled water). The mixture was then transferred to ten polypropylene reactors, and the reaction temperature was kept at 80 °C, and the ten samples were kept at various crystallization periods (1, 3, 7, 16, 25, 44, 72, 96,136, and 160 h). After the crystallization period, the solid was separated by filtration and then washed with distilled water. The samples were dried overnight at 100 °C, thus forming zeolites X and A revealing improvement in crystallinity with the reaction time (Moisés et al. 2013). A similar procedure was followed using microwave energy compared to the fusion step, BFA mixed with NaOH and $BaCl_2{\cdot}2H_2O$ with an S/L ratio of 1:10, and the resulting mixture was subjected to microwave treatment of 900 W and then hydrothermally cured at hydrothermal conditions. The barium-impregnated BFA zeolite has an average adsorption capacity of 45.02 mg g^{-1} compared to Ba-impregnated zeolite blended with alumina, which has 48.59 mg g^{-1}. The zeolite-A ($Na_{12}Al_{12}Si_{12}O_{48}{\cdot}27\,H_2O$) was synthesized from BFA using fusion-assisted hydrothermal step. The calcined BFA at 600 °C was prepared for silica extraction by the alkali fusion step of NaOH at 550 °C for 4 h. The obtained product is stride using DI water, and then this solution is added to the aluminate solution to synthesize Zeolite-A. The initial large surface area property of BFA is affected by the application of pre-treatment using HCl (10%) (Jangkorn et al. 2022). Hydrothermal synthesis is the easiest conventional method for the conversion of BFA into zeolites. Thus, forming sinks for harmful cations from wastewater is depicted in the following part of the manuscript.

Table 12.2 The BFA zeolite synthesis parameters and their applications in adsorption studies

Reference	SiO_2/Al_2O_3	Zeolite synthesis parameters				Zeolites formed	Metal ion adsorbed	Maximum adsorption capacity	Remarks
		Method	*T* (°C)	*t* (h)	Other conditions				
Purnomo et al. (2012)	22.71	Fusion-assisted hydrothermal	120	18–48	Fusion step at 773 K for 1 h, Si/Al ratio adjusted to 1.8	Na-A and Na-X			Fusion step silica extracted and treated hydrothermally to obtain zeolite
Oluyinka et al. (2020)	–	Alkali fusion technique and microwave hydrothermal treatment	–	–	Microwave energy of 900 W, frequency 2.5 GHz for 20 min	–	–	30.86 mg g^{-1} and 19.92 mg g^{-1}, respectively	Adsorptive removal of p-nitroaniline and nitrobenzene are studied
Jangkorn et al. (2022)	1.48 (Si/Al)	Alkaline fusion followed by hydrothermal	80	72	Pretreatment by calcination is carried out 600 °C	Zeolite-A	Lead	625 mg g^{-1}	CaO would interfere with the zeolite crystal nucleation, so it must be destroyed
Moisés et al. (2013)	30.78	Hydrothermal method	80	72–160	Silicon is extracted by alkali fusion at 40 min at an alkali ash ratio of 1 and a temperature of 550 °C	Zeolite-A			Using the alkali fusion method, zeolite A was observed to form from BFA with a crystallization period of 25 h
Oliveira et al. (2019)	1.71 (Si/Al)	Hydrothermal method	100	24	Calcination is carried out at 600 °C at 8 h	Zeolite A	Copper	142 mg g^{-1}	The maximum adsorption capacity was achieved by the addition of Al and hydrothermal treatment, which

									alters the zeolitic material
Purnomo et al. (2012)	1.8 (Al/Si)	Alkali fusion method	90	30	Weight ratio of 1:1.2 = BFA: NaOH and heated at 773 K for 1 h	Na-X	Cadmium		The silica content is extracted from BFA to initiate zeolite crystallization
Donphai et al. (2022)	–	Alkaline fusion with sodium carbonate	100	24	Calcination is carried out 85 °C at 1 h	MCM-41	–	0.679 $g_{VOC}/g_{adsorbent}$	MCM-41 prepared with bagasse ash was successfully used to remove Volatile organic compounds, which showed better results than that of commercial adsorbents
Shah et al. (2013)	30 (Si/Al)	Microwave-assisted method			Energy –900 W Frequency 2.45 GHz and for 17 min	Ba-impregnated zeolite	–	48.59 mg g^{-1}	The synthesized zeolite is effectively used for the sorption of aniline

12.2.1 Application of Synthesized Zeolite in Heavy Metal Removal

The synthesized zeolites possessing tetrahedrons in their framework filled with Na^+ cation are replaced with cations of higher order, thus luring cations into their cages. The pore properties along with the large surface area make zeolites derived from BFA to be excellent adsorbents against heavy metals. An investigation carried out on copper sorption studies conducted on fusion-assisted hydrothermal synthesized zeolite revealed acidic environment pH <2.5 leads to protonation causing cease of adsorption; however, a perfect pH at 4.5 recorded maximum efficiency of Cu^{2+} adsorption. A maximum adsorption capacity of 142 mg g^{-1} was obtained in the case of copper adsorption (Oliveira et al. 2019). A similar investigation was carried out using lead ion at varied dosages of 10–70 mg L^{-1} and varying adsorption parameters like sample volume, shaking speed and dose, contact time, and pH the adsorption characteristics of zeolite are carried out. The adsorption studies revealed an optimum condition for 100% efficiency toward lead removal, that is, zeolite-A demonstrated 100% removal when subjected to 0.02 g dosage, 2 h contact time, pH of 5, and 10–70 mg L^{-1} (Jangkorn et al. 2022). A similar investigation was carried out on the use of BFA-synthesized MCM-41 used as a low-cost adsorbent. The obtained MCM-41 functionalized with carbon and zinc revealed enhanced adsorption toward VOCs like formaldehyde, hexane, and toluene. These applications have revealed the true potential of BFA zeolite in environmental applications (Donphai et al. 2022).

The BFA turned into zeolites revealed their excellent adsorption properties, thereby suggesting their potential toward a sustainable environment and cleaner productions.

12.3 Conclusions

The current work aims at exploring the potential applications of BFA in environmental engineering practices. BFA has been proven its widespread applications in the cement and construction industry. However, the BFA's true potential is yet to be explored further as an adsorbent. The key to the synthesis of low-cost adsorbents is the availability of low-cost precursor materials. The BFA is an agricultural solid waste with a good quantity of unburnt carbon and siliceous compounds. A step toward sustainability is through the conversion of wastes to resourceful materials, BFA is one such material available in abundance, which can be utilized in the synthesis of zeolites. Furthermore, these synthesized zeolitic materials can be used in the decontamination of wastewater contaminated with heavy metals. The composition of BFA has proven its effectiveness in the construction industry due to its pozzolanic nature. However, the benefits offered by BFA in environmental fields are more sustainable, economical, and advantageous in multiple folds. The renewability, low cost, excellent adsorption capacity, and regeneration capability make the BFA a one-stop solution for major environmental issues related to heavy metals. Furthermore, there is a need for improvements as complete conversion, regeneration, and possible leaching of ions demand further investigations.

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Extraction of Lignin from Various Agricultural Biomass: Its Characterization and Applications

13

Bing Wang, Yating Zhang, Yaping Zhang, and Ruolong Pan

Abstract

With the continuous transformation of social consumption demand to the direction of green and sustainable development, the demand of humans for green and renewable resources is increasing. Lignin, as a naturally synthesized polymer, is widely found in plant cell walls. It has high carbon content and energy storage, which is renewable. If used reasonably, it is expected to become one of the most available renewable biological resources. At present, although there is a large amount of lignin in agricultural wastes, its extraction and valid utilization are limited due to its structural complexity and heterogeneity. Therefore, it is of great significance to effectively and rationally utilize and realize the high-value conversion of lignin. To further study how to efficiently extract lignin from agricultural biomass and its characterization and application, the pretreatment methods of agricultural waste for lignin extraction are introduced at the beginning of this chapter, including physical, chemical, and biological treatments. Then, the traditional methods of lignin extraction from different agricultural biomass (such as high-boiling alcohol solvent extraction and organic solvent extraction) are described. Thirdly, some typical characterization techniques of lignin are introduced, including nuclear magnetic resonance (NMR) and two-dimensional nuclear magnetic resonance (HSQC NMR) methods. In terms of application, lignin has been applied to different fields due to its good dispersion, adhesion, and surface activity, such as industrial, agricultural, and medical fields. Besides, lignin is also used as a binder, dispersant, and surfactant. In general, lignin, as a natural renewable polymer, has a high possibility of industrial production due to

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its abundant resources and low price. In the pursuit of green environmental protection and sustainable development today, it has become a key research hotspot.

Keywords

Agriculture biomass · Lignin · Extraction · Characterization · Application

13.1 Importance of Lignin Extraction

In 1838, when French scientist P. Payen separated cellulose from wood, he discovered a high-carbon polymer compound with high carbon content, which was formed by connecting three phenylpropane units through carbon-carbon double bonds and ether bonds. The compound was later named "lignin." The six carbon atoms on the three carbon chains are attached to the benzylene ring. Due to the difference in the number of methoxyl groups on the benzene ring, lignin can form three structures: H-type, G-type, and S-type. The structure of lignin extracted from different sources of biomass is completely different. The lignin extracted from coniferous plants is usually H-type, while S-type and G-type are related to broad-leaved plants. Lignin mainly exists in wooden, herbs, and all vascular plants. As a renewable and degradable natural resource, it is extremely rich in nature and is the second largest biological energy in the world after cellulose (Gallezot 2012). Thus, the extraction of lignin is essential for its resources.

Lignin, cellulose, and hemicellulose constitute the main components of plant skeleton—lignocellulose. Among them, lignin plays a dual role of binding fibers and making fibers stiff. In plants, lignin and hemicellulose together fill the cell walls as intercellular substances, thus connecting adjacent cells and playing the role of lignification (Liao et al. 2020). The lignified cell wall enhances the strength of the plant and can resist the invasion of microorganisms, and the water permeability and water holding capacity of the cell wall are also improved. In addition, lignocellulose is a renewable resource, which can curb global warming and energy crisis and blaze a new trail for many environment-friendly product streams.

Lignin not only plays an important role in plants but also has broad prospects in other fields. There are active groups such as aromatic group, methoxy group, carbonyl group, alcohol hydroxyl group, phenol hydroxyl group, and carboxyl group in the structural unit of lignin, which also has the characteristics of thermal stability, biocompatibility, and low cost. Therefore, lignin has been used in many fields as a promising adsorbent (Cha et al. 2020), such as adhesives, cement, flame retardant, antioxidants, etc. At present, lignin has been widely used to prepare phenolic resin, polyurethane, epoxy resin, ion exchange resin, and other materials. As a filler, it is used to modify rubber, polyolefin, starch, protein, and other fossil resource bases and biomass. Based on polymer materials, it has successfully developed new materials with great application potential, such as adhesives, films, fibers and nanofibers, hydrogels, etc. Meanwhile, lignin and its derivatives can be used as surfactants, flocculants, etc. It can also be used in oil extraction, asphalt emulsification, wastewater treatment, pesticide slow release, antiviral and antitumor drug raw materials, drug carriers, etc.

Lignin is difficult to be separated or effectively utilized from biomass due to its uneven properties and complex chemical structure. At present, only 5% lignin is used, and the utilization rate of lignin is lower than those of cellulose and hemicellulose. In view of the fact that lignin is an extremely rich natural resource, people pay more and more attention to the research, development, and utilization of lignin. Nowadays, there has been a lot of lignin in the by-products of wood hydrolysis industry, paper industry wastewater, and agricultural wastes. However, their utilization rates are very low, which is considered as a great waste of resources. For this reason, in recent years, the research on high-value utilization of lignin has been increasing. Extracting lignin from crops or industrial by-products can not only solve the problem of waste on environmental pollution, but also realize the resource utilization of lignin, promoting the sustainable development of industry and agriculture.

13.2 Pretreatment of Agro-Waste

With the increase of population, the amount of agricultural waste is increasing year by year all over the world. As an important renewable resource, it has great potential and value in resource utilization. In the past few decades, there have been many studies on obtaining value-added products by developing and improving the treatment methods of agricultural wastes (Rajagopal and Liu 2020). Among them, the research on the treatment and value-added transformation of lignocellulosic biomass is particularly outstanding. However, in the value-added process of biomass, the obstinacy of lignocellulose is the main obstacle to the comprehensive utilization of lignin. The pretreatment process of agricultural waste is a key step to convert biomass into other valuable by-products such as sugar and biofuel. The different pretreatment methods can be adopted to overcome the obstinacy of lignocellulosic biomass and accelerate its decomposition into separate components cellulose, hemicellulose, and lignin. Therefore, to separate and extract lignin from agricultural wastes, pretreatment of lignocellulosic biomass is essential. This section outlines the pretreatment process of lignocellulosic biomass, providing a reference for the resource utilization of agricultural waste in the future.

Lignocellulose has great potential in the production of biomolecules, chemical products, and biofuels. Through the pretreatment of lignocellulose and conversion into other valuable by-products, it is conducive to the resource utilization of agricultural waste. Its process flow is shown in Fig. 13.1. Firstly, the biomass is crushed and sieved to make the solid material particles smaller and the specific surface area increases, so as to facilitate transportation, mixing, and subsequent treatment. Secondly, appropriate methods (physical, chemical, physicochemical, and biological pretreatment methods) are adopted to pretreat the biomass. Lignin, cellulose, and hemicellulose are separated to improve the utilization rate of biomass resources.

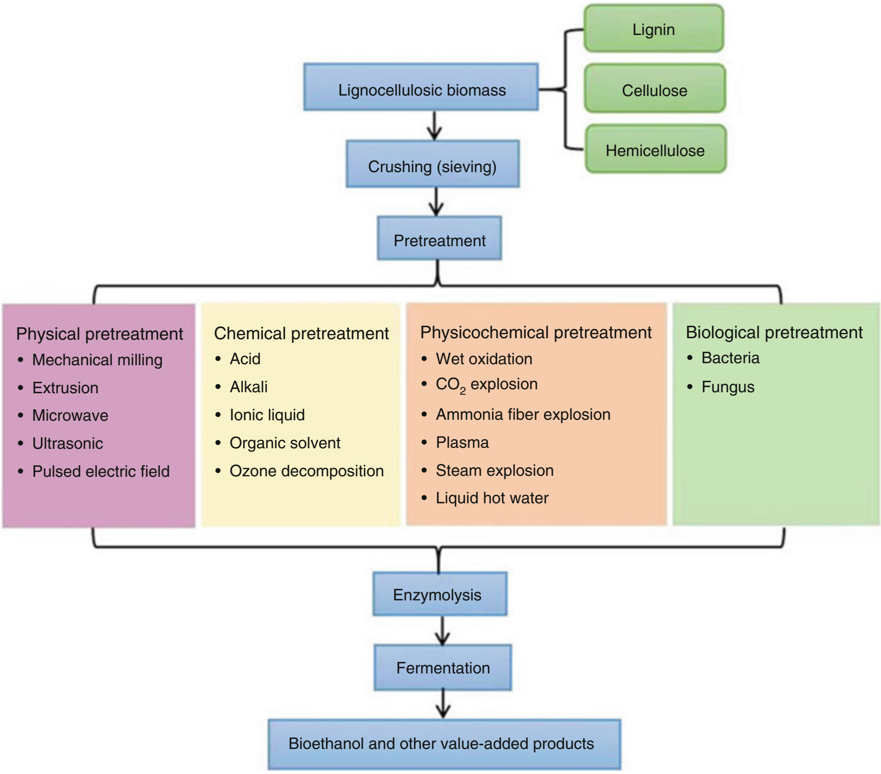

Fig. 13.1 Overview of different pretreatment processes for lignocellulosic biomass

Finally, cellulase hydrolysis, fermentation, and other processes are used to further decompose and transform biomass and change its original properties to prepare value-added products such as bioethanol.

Among them, the choice of lignocellulose pretreatment method is very important, which is the key step to decompose the three components and efficiently convert them into bioenergy. Therefore, before adopting a specific pretreatment method, many factors should be considered. The pretreatment methods of biomass usually include physical, chemical, physicochemical, and biological pretreatments. The pretreated biomass can reduce the operating, capital, and biomass costs of the downstream treatment process. Next, different types of pretreatment methods will be discussed in detail as follows.

13.2.1 Physical Pretreatment

Physical pretreatment of lignocellulose is mainly to reduce polymerization degree and particle size through physical and mechanical methods. It can further increase the surface area and accessibility of enzymatic hydrolysis, making the subsequent treatment process easier and more effective. Physical pretreatment methods include mechanical grinding, extrusion, microwave, ultrasonic, pulsed electric field, etc. These methods have the advantages of simple operation, environmental protection, and few toxic compounds. However, the price of the processing equipment is expensive, not only the energy consumption is large, but also affected by the pressure and the treatment temperature. Ultrasonic and microwave radiation for biomass decomposition, in particular, are not suitable for large-scale applications. It is worth noting that when physical pretreatment is applied together with chemical methods, it shows a synergistic effect and can obtain higher output (Tu and Hallett 2019), such as a plasma pretreatment method. In a laboratory scale, plasma pretreatment was used to greatly increase the yield of reducing sugar, and argon-low temperature atmospheric pressure plasma (CAPP) was used to treat Chlorella. It was found that a low dose lasting for 30 s could significantly increase colony formation and biomass productivity (Almarashi et al. 2020).

13.2.2 Chemical Pretreatment

Chemical pretreatment is to add some chemicals or water to treat biomass, such as acid, alkali, organic solvent, ionic liquid, and ozone. It promotes hydrolysis or delignification reaction by destroying the chemical structure of biomass waste. However, it will also weaken the bonding (covalent bond) and intermolecular interaction (hydrogen bond), leading to the deterioration of the polymer structure (Li et al. 2010). Among them, the application of chemical substances such as acid, alkali, ozone, and organic solvents can significantly improve the processing efficiency. However, if these chemical reagents are not removed in time, the risk of pollution will increase. Moreover, this process is accompanied by the production of harmful inhibitors, which leads to the risk of secondary pollution. It is not environmentally friendly and economical in industrial applications and should be combined with physical methods. For example, at present, physicochemical methods such as liquid hot water, steam explosion, ammonia fiber explosion, and CO_2 explosion have been successfully applied to the pretreatment of lignin, which have high economic benefits and can effectively reduce the risk of secondary pollution.

13.2.3 Physicochemical Pretreatment

Physicochemical pretreatment is a new pretreatment method combining physical and chemical methods, which has a synergistic effect. It can solve the problems of high energy consumption in the physical pretreatment process, and the whole process will be affected by various environmental factors and operating conditions, but also it can avoid the generation of harmful inhibitors in the chemical pretreatment process, with high cost-effectiveness. The treatment methods include wet oxidation, CO_2 explosion, ammonia fiber explosion, plasma, steam explosion, and liquid hot water. Even so, physicochemical pretreatment methods still have some defects. For example, in the process of ammonia fiber explosion treatment, the recovery cost of ammonia is high, it is not suitable for high lignin biomass, the effect on cork biomass is poor, and the plasma treatment requires professional equipment. Up to now, there is no single pretreatment method that can completely delignify biomass in an economical and environmentally friendly way. Although the combination of physicochemical methods has been successful to a certain extent, a great deal of research is needed to give full play to the potential of the combined pretreatment methods.

13.2.4 Biological Pretreatment

Biological pretreatment refers to the pretreatment with biological agents, namely, bacteria, fungi, or effective combinations, such as *Clostridium cellulosum*, *Bacteroides*, *white rot fungi*, *brown rot fungi*, *Actinomycetes,* and *Basidiomycetes*, which can generally produce enzymes that degrade hemicellulose, cellulose, and lignin. Although the physicochemical methods are very mature, the biological methods not only have more prospects in reducing waste liquid but also have broad application prospects in the degradation of lignocellulose and the formation of value-added products. Biological pretreatment has the advantages of high cost efficiency, environmental protection, minimal energy demand, and consistent with the concept of sustainable development. However, this method still faces great challenges in terms of technology and economy. For example, pH, temperature, and microbial activity will affect the biological pre-processing process (Sharma et al. 2019). Therefore, it is not widely used in industry, and more environmentally friendly treatment methods need to be improved and developed in subsequent research.

Up to now, conventional pretreatment methods have been used in the pretreatment of each stage of biomass value-added process. However, these methods have high operating costs, harsh process conditions, and the risk of secondary pollution. Currently, an efficient and environmentally friendly pretreatment method for separating cellulose and hemicellulose from lignin has not been established. Therefore, analyzing and comparing the advantages and disadvantages of pretreatment methods will be beneficial to further develop more efficient and widely applied technologies. Table 13.1 summarizes and compares the advantages and disadvantages of lignocellulose pretreatment methods.

13.3 Methods of Lignin Extraction

For the subsequent process, the extraction of lignin is very important. Impurities will not only lead to degradation of the separation and purification effect but also affect the recovery and reuse of the solvent. If the extraction method is not correct, it can also lead to unnecessary losses. Lignin extraction is divided into two main types according to the perspective of components. One is to obtain lignin by dissolving

Table 13.1 Comparison of advantages and disadvantages of lignocellulose pretreatment methods

Preprocessing method types		Advantages	Disadvantages
Physical pretreatment	Mechanical milling	Simple operation, reduced particle size and cellulose crystallinity, without producing any toxic inhibitors	High energy and power requirements for hardwood, requiring high-cost equipment
	Extrusion	Moderate temperature requirements, low yield of degradation products, less formation of harmful inhibitors	Failure of thermoregulation technology, insufficient cooling capacity, dwell time limitation
	Microwave	Simple operation, energy saving, short time, minimal formation of toxic inhibitors, no pollution	High investment, production of fermentation inhibitors
	Ultrasound	Short process duration, non-polluting, mild process conditions, no recycling chemicals and waste disposal, no fermentation inhibitors	Long time ultrasonic treatment may have adverse effects on hydrolysis, energy intensive process requires biomass volume reduction and can only be used under low solid load
	Pulsed electric field	Low energy consumption, economy, environmental protection, no production of fermentation inhibitors, fast method, mild conditions	Energy intensive process, not suitable for all types of substrates
Chemical pretreatment	Acid	Simple and convenient, low cost, high yield of xylose, lignin and hemicellulose are not easy to dissolve, the response time is short, and the processing efficiency is high	With fermentation inhibitor generation, acid corrosion reactor, high cost
	Alkali	Simple processing process, less sugar degradation, increased surface area, reduced degree of polymerization and crystallinity	Softwood has low digestibility, residence time too long, the recycling cost of chemical reagents is high
	Ionic liquid	The reaction conditions are mild, no toxic inhibitors are produced, and the cellulose is dissolved efficiently	The cost of ionic liquid is high, enzyme activity will be suppressed, and the treatment of high -viscosity solution is difficult
	Organic solvent	After treatment, the quality of the lignin is high, the solvent distillation is easy to recover, and there are few toxic inhibitors formed	Organic solvents are high in price, need to recycle. Solvents, and the treatment conditions are strict

(continued)

Table 13.1 (continued)

Preprocessing method types		Advantages	Disadvantages
	Ozonolysis	Low energy requirement, efficient lignin removal, the reaction can be performed directly at room temperature and will not produce toxic inhibitors	Ozone demand is large, and the cost of oxidant is high
Physicochemical pretreatment	Wet oxidation	High lignin removal efficiency, less inhibitor formation, relatively low energy requirement due to exothermic process	High temperature requirements, high catalyst costs, and high operating costs
	CO_2 explosion	Low carbon dioxide cost, little impact on the environment, no toxic inhibitors, nonflammable, high conversion rate	Low lignin solubilization, high pressure conditions, high cost of CO_2 processing, not suitable for industrial use
	Ammonia fiber explosion	Efficient removal of lignin, less inhibitor formation, no need for washing and neutralization, short reaction time	Ammonia recovery costs are high, not suitable for high lignin biomass, less effective for softwood biomass
	Plasma	Short process duration, no pollution, mild process conditions, do not need to recycle chemicals, no fermentation inhibitors will produce	Professional equipment required
	Steam explosion	Small environmental impact, high energy efficiency, no recovery cost	Long residence time, it is easily affected by various environmental factors, and toxic inhibitors will also be generated
	Liquid hot water	No catalyst or chemical substance is involved, no toxic inhibitor is formed, and the process cost is low	High energy consumption, large water demand, will form a large number of low-concentration products
Biological pretreatment	Bacteria and fungi	Low energy consumption, environmental protection, no need for chemicals or catalysts, no formation of toxic inhibitors, sustainable	Time-consuming, partial hydrolysis of hemicellulose, most microorganisms not only dissolve or consume lignin, but also dissolve cellulose and hemicellulose, the process is affected by physical conditions

other components, and the other is to use solvents to dissolve lignin, thus separating it from other components to achieve the extraction effect. Common extraction methods include acid precipitation, alkali precipitation, ultrafiltration, organic solvent, and high-boiling alcohol method. The high-boiling alcohol method and the organic solvent method are widely used in the extraction of lignin because they are in line with the green concept, have high extraction efficiency for lignin, solvent recovery, and reuse efficiency.

13.3.1 High-Boiling Alcohol Solvent Extraction

High-boiling solvent (HBS) extraction is a method of extracting lignin, which is essentially an organic solvent method characterized by a high boiling point of the solvent. Compared to organic acids or low boiling point organic solvents, little evaporation loss was obtained during cellulose washing (Gnana Prakash et al. 2022). This method involves the separation of water-insoluble lignin from cellulose by dissolving it in a high-boiling alcohol solvent under heated conditions. Then obtain lignin through water precipitation method. The original structure and activity of the lignin can be better preserved, and the high-boiling alcohol solution after use is recovered by reduced pressure distillation for reuse. The utilization efficiency of high-boiling alcohols is over 98%. High-boiling alcohol lignin has very low sugar and ash content. It has a high chemical reactivity and contains a lot of reactive groups. In the preparation of lignin derivatives and polymer materials, high-boiling alcohol solvent extraction has been widely used. The hemicellulose in the plant material is degraded during the process of high-boiling alcohol solvent extraction. This will cause residual sugar to dissolve in the waste stream. If the residual sugars are not removed, it will limit the recycling of high-boiling alcohols.

The specific extraction process is as follows. Firstly, rice husk with 70%–90% 1,4-butanediol aqueous solution is mixed with the autoclave. The reaction is heated to 200–220 °C for 1.0–3.0 h at a certain solid material to solvent mass ratio. Water precipitation was used to extract the insoluble RHL from of the mixture (Chen and Cheng 2008). High purity lignin was extracted from waste residue of straw biological refining plant by alkali extraction. What is different from the previous method is the addition of cosolvent glycol (EG). At 190 °C for 300 min, the recovery of lignin was 94%. The lignin content (purity) was 92%. It has been proved that adding EG can improve the solubility of lignin in solution, and the lignin yield and recovery rate were higher than that of soda ash method (Lo et al. 2021). In addition, using 1,4-dioxane as the solvent, lignin was extracted using an enhanced HBS technique. The HBS lignin sample that was obtained had a lower ash percentage (approximately 0.25%) than other lignin samples. Moreover, many hydroxyl groups can be found in HBS lignin, indicating that it has potential value as a substitute for polyols in the synthesis of polyurethane (Jia et al. 2015). These methods extracted HBS with high content and low ash content. However, in order to achieve higher extraction effect, a certain amount of co-solvent can be added to the alcohol solvent to lower the reaction temperature. The lignin separation efficiency can also be significantly improved by mixing concentrated sulfuric acid and acetic acid in a certain ratio as a compound catalyst. And proper extension of holding time can improve lignin yield. All these optimization methods are expected to broaden the prospects of practical application of lignin extraction by the high-boiling alcohol method.

13.3.2 Organic Solvent Extraction

Among various methods for lignin extraction, organic solvent extraction is the first and most efficient method. This method was adopted as early as the end of the nineteenth century as a pulping method that could obtain both pulp and lignin at the same time. However, it was eliminated due to the low recovery rate of organic solvents, high cost, and the lack of marketability of the extracted lignin at that time. In the 1980s, organic solvent extraction became a popular technique again.

From the perspective of integrated lignin biomass utilization, organic solvent extraction provides a pathway for the biorefining of biomass. Brauns natural lignin and Nord lignin were the lignin extraction methods that emerged in the 1940s. The process is mainly to extract the wood powder through 100–200 mesh with water and ether and then extract with ethanol of 95% purity to obtain the lignin concentrate. But it does not represent the original lignin due to the excessive impurities it contains. Björkman lignin is also the classic lignin extraction method. The defatted wood flour is ball-milled for a certain length of time and then extracted and concentrated with organic solvents. However, at this time, the concentrated lignin contains more sugars and needs to be purified to obtain lignin of higher purity. One of the most classic lignins is that obtained by 1,4-dioxane extraction following ball milling and the Björkman technique. Although mechanical processing may somewhat modify the lignin structure, its chemical properties are similar to those of natural lignin. Nowadays, there are many methods of lignin extraction with organic solvents, but the general extraction process is similar. Due to the diversity of organic solvents and the different extraction effects, a variety of organic solvents are used in the treatment process, such as acetic acid, ethanol, methanol, acetone, and peracetic acid. In this procedure, water and organic liquids are combined in various ratios before being added to the biomass. The lignin and some hemicellulose were dissolved from the mixture by heating it, leaving behind a rather pure cellulose residue. Catalysts can be added to enhance the delignification process. However, high temperature and pressure conditions can affect the operation process. Lignin is a natural polymer with different structures in different plant fiber raw materials. The structure of lignin varies even in different parts of the same raw material. Thus, lignin itself is structurally massive and complex, and lignin is chemically extremely unstable. Chemical changes occur when affected by chemical reagents, temperature, and acidity. Even under milder conditions, condensation can occur. So far, there is no method to obtain the natural lignin. This has caused some difficulties for the lignin research, and there have been still many technical difficulties for full industrialization, making its application highly restricted. Thus, based on the abovementioned drawbacks of organic solvent method for lignin extraction, the lignin yield, separation efficiency, and operating conditions should be further improved in future practical applications. Moreover, the technical optimization is recommended to achieve the higher extraction efficiency with less energy and chemical consumption.

13.4 Characterization Techniques

Lignin is a particular kind of organic polymer. Phenylpropane structural units make up its three-dimensional spatial structure. The purpose of characterizing lignin is to study its internal structure, composition, and morphology. For chemical substances, the structure determines the properties, and the properties are derived from the structure. Currently, lignin molecular structure is studied by wet chemical methods, including potassium permanganate oxidation, thioglycolysis, nitrobenzene oxidation, etc. Although wet chemical methods can obtain structural information about lignin, they are incomplete in characterizing functional groups. Spectroscopic methods include UV spectroscopy, Fourier infrared spectroscopy, and nuclear magnetic resonance spectroscopy. NMR is widely used in lignin characterization due to the advantages of providing abundant structural information and good characterization effect. This chapter will introduce the NMR method and HSQC NMR method for lignin characterization.

13.4.1 Advanced Nuclear Magnetic Resonance (NMR)

Nowadays, NMR has rapidly developed into a powerful tool for determining the structure of organic compounds and played a crucial role in wood chemistry in particular. Since the 1970s, the use of superconducting NMR instruments with strong magnetic fields has greatly increased the sensitivity of the instrument, leading to the rapid expansion of its applications in the field of biology.

To describe lignin, nuclear magnetic resonance spectroscopy has been employed for a while (Strahan et al. 2022). Nuclear magnetic resonance spectra include proton, carbon, phosphorus, and two-dimensional heteronuclear single-quantum coherence spectra (^{1}H, ^{13}C, ^{31}P, and 2D HSQC). NMR can reveal the overall structure of lignin. The main common NMR spectra commonly used in lignin research include ^{1}H NMR, ^{13}C NMR, 2D HSQC NMR, and quantifiable 31P NMR, the characteristics of each spectrum are shown in Table 13.2. It is well known that hydrocarbons are the main components of organic compounds and polymeric materials. The most often employed NMR spectra to analyze material structure and characteristics are hence ^{1}H NMR spectra and ^{13}C NMR spectra. In this section, these two common NMR spectra will be introduced.

^{1}H NMR spectroscopy: ^{1}H NMR spectroscopy is an older technique for characterizing lignin, and the high natural abundance of ^{1}H nuclear (about 99.98%) gives the technique high sensitivity, small sample size, and a short

Table 13.2 Properties of common NMR spectra

Isotopes	γ	Resonance frequency at 11.7 T	Natural abundance (%)	Comparative sensitivity
^{1}H	100	500 MHz	99.98	1
^{13}C	25	125 MHz	1.1	10^{-5}
^{15}N	−10	50 MHz	0.37	10^{-7}
^{31}P	40	203 MHz	100	0.07
^{29}Si	−20	99 MHz	4.7	10^{-3}

Table 13.3 Chemical shifts of protons in common groups

Proton category	δ/ppm	Proton category	δ/ppm
$R–CH_3$	0.9	Ar–H	7.3 ± 0.1
R_2CH_2	1.2	RCH_2X	3–4
R_3CH	1.5	$O–CH_3$	3.6 ± 0.3
$=CH–CH_3$	1.7 ± 0.1	–OH	0.5–5.5
$\equiv C–CH_3$	1.8 ± 0.1	$–COCH_3$	2.2 ± 0.2
$Ar–CH_3$	2.3 ± 0.1	R–CHO	9.8 ± 0.3
$=CH_2$	4.5–6	R–COOK	11 ± 1
$\equiv CH$	2–3	$–NH_2$	0.5–4.5

acquisition time (about minutes). Chloroform and other solvents can be used in ^{1}H NMR analysis of lignin. The chemical shifts, coupling constants, and peak splitting of different protons in the oxygen spectrum can provide important information on the structure of lignin. In the hydrogen spectrum, the peak area of hydrogen is proportional to the number of hydrogen atoms. Such quantitative relationships are difficult to be obtained in IR, UV, and mass spectrometry. Measuring the ratio of the number of hydrogen protons in various functional groups is essential to infer the structural formula. Therefore, hydrogen spectroscopy has become an important tool for the quantitative analysis of lignin. Due to the shielding effect of different protons in the compound molecule, the absorption peaks appear in different positions of the NMR spectrum. However, the difference in position caused by this shielding effect is small, and it is difficult to measure its absolute value precisely. Thus, a standard is needed for comparison. Tetramethylsilane ($(CH_3)_4Si$) is commonly used as a standard, and the position where its absorption peak appears is artificially set to zero. The difference between the position of the absorption peak of a proton and the position of the proton absorption peak of a standard substance is the chemical shift of the proton, often expressed as "δ." Table 13.3 shows the chemical shifts of protons in common groups. Since NMR test samples are prepared as solutions or pure liquids. Thus, solvent effect and the formation of hydrogen bonds have sometimes significant effect on the chemical. Protons that form hydrogen bonds have a larger chemical shift than those that do not, because the formation of hydrogen bonds decreases the density of the electron cloud outside the nucleus. For example, the -OH peak of ethanol is $\delta = 4.6$ under normal conditions, and the chemical shift increases as the association is enhanced. This is a frequent concern in the characterization of extracted lignin

^{13}C NMR spectroscopy: ^{13}C NMR spectroscopy is similar to proton nuclear magnetic resonance (^{1}H NMR) and can identify carbon in organic compounds just like ^{1}H NMR. Therefore, ^{13}C NMR becomes one of the important tools to understand the structure of lignin. ^{13}C NMR can only detect the isotope of ^{13}C (which naturally contains only 1.1%). ^{12}C is not detectable by NMR because it has zero spins. For lignin, ^{13}C NMR spectra have several advantages over ^{1}H NMR spectra: (1) ^{13}C-NMR can reveal all carbon chain structures in the lignin structure; (2) ^{13}C NMR has a wider range of chemical shifts compared to ^{1}H NMR spectra, which can effectively reduce signal stacking; and (3) negligible spin-spin coupling interference. However, ^{13}C NMR spectra have a longer acquisition time than ^{1}H NMR spectra. Molecular weights of various lignins can be estimated using ^{13}C NMR. Capanema et al. (2004) quantitatively analyzed different lignin structures in MWL by ^{13}C NMR spectroscopy. Moreover, the results obtained are very close to those obtained by other methods, and the detailed calculation process is described in the literature.

13.4.2 Two-Dimensional Nuclear Magnetic Resonance (HSQC NMR)

Two-dimensional NMR is a powerful tool for accurate analysis of complex organic compounds. Techniques for one-dimensional NMR, such as ^{1}H and ^{13}C NMR, frequently experience substantial signal overlap. This issue can be resolved using 2D HSQC NMR, which is especially useful for identifying the presence of lignin subunits and lignin-carbohydrate complexes. The biggest difference between two-dimensional NMR spectra and one-dimensional NMR spectra is the addition of an independent frequency dimension. This makes spectral simplification possible. Two-dimensional NMR spectra eliminated spectral overlap, making spectral allocation easier and providing more information (Lhoste et al. 2022). By introducing NMR experiments with two-time variables, two-time variable NMR studies enable 2D NMR to reveal crucial characteristics like chemical shifts and coupling constants in the two-dimensional plane. The problem of crowding and overlapping of spectral lines is perfectly solved while still providing important information about the interaction between spin nuclei. Therefore, 2D NMR has an irreplaceable position in accurately resolving the structures of complex organic molecules, especially sugars, proteins, and nucleic acids.

Two-dimensional heteronuclear single-quantum carbon-hydrogen correlation spectroscopy (2D HSQC NMR spectroscopy) is an important modality in the structural analysis of lignin. 2D HSQC NMR spectroscopy provides important structural information by well-distinguishing overlapping signal peaks in the hydrogen and carbon spectra. The 2D HSQC NMR spectrum of lignin can be divided into three regions, namely, the aliphatic region, the side chain region, and the aromatic ring region. Of these, the signals associated with the aliphatic region are mainly from the signals of the methyl (CH) and methylene (CH_2) side chains and the acetyl groups of lignin. The side chain region (also known as the linkage region) can distinguish well between lignin side chain linkage types (e.g., β-O-4, β-β, β-5, β-1, etc.), methoxy, and carbohydrate linkages to lignin (e.g., benzyl ether bond, etc.). The relative proportions of different linkages can be calculated based on the integral intensity of the signal at the α-position of each linkage. The aromatic ring region allows a good distinction to be made between the basic chemical building blocks of lignin, the signals associated with some of the terminal groups (e.g., p-hydroxycinnamic alcohol terminal group and cinnamaldehyde terminal group), and some of the linkage bonds. Complex signals in aliphatic carbon-oxygen related regions with many overlapping signals are of little significance for lignin structure resolution. Therefore, it is generally not analyzed. The following example is a more representative assay step. A 2D HSQC NMR spectra was captured in the HSQC experiment using lignin that was dissolved in 0.5 mL of DMSO-d_6 (dimethyl sulfoxide) at a concentration of 90 mg. The ^1H and ^{13}C dimensions have spectral widths of 5000 and 20,000 Hz, respectively. Using a 1.5 s cycle delay, 1024 ^1H dimensions of complex points were gathered. There were 64 transients total, and the ^{13}C dimension was always recorded in 256-time steps. The central solvent (DMSO) peak was used as an internal chemical shift reference point (δ_C/δ_H 39.5/2.49). Data processing was performed using standard Bruker Topspin-NMR software (Moghaddam et al. 2014). Two-dimensional NMR techniques also plays an important role in paper making, and this technique has been successfully applied to the characterization of lignin structure in the process of wood modification. The outcomes demonstrated that under the catalysis of C1 and C2, the biphenyl (5–5) and stilbene structures of lignin residue in pulp were selectively degraded. But the degradation of the β-O-4, β-5, and β-β structures was less severe. Therefore, in carbon-oxygen in two dimensions for the structural characterization of lignin, NMR analysis is a crucial analytical technique (Chen et al. 2003). Table 13.4 shows the attribution of the main 2D NMR ^{13}C-^1H HSQC chemical shifts in lignin.

13.5 Application of Lignin

The application of lignin began in the nineteenth century. In recent decades, lignin has been widely used in industrial, agricultural, and medical industries such as dispersants, adhesives, and even organic fertilizers made from lignin. They have made great contributions to plant growth. Based on the new properties and application functions of lignin-based multielement materials, the current application of lignin will be elaborated in this section.

13.5.1 Industrial Applications

Lignin itself is viscous and can be directly used as a binder. Lignin in natural plants acts as a binding agent, distributing around the fibers and between the tiny fibers

Table 13.4 Attribution of major chemical shifts of 2D NMR ^{13}C-^{1}H HSQC in lignin

Structural units	δ_C/δ_H	Attributions
$-OCH_3$	56.0/3.8	Methoxy structure on the benzene ring
A_α	71.6/4.7	C_α-H_α in the structure of SU β-O-4(A)
A_β	80.5/4.4&83.9/ 4.3	C_β-H_β in the β-O-4(A) structure of the connected G unit
A_γ	60.4/3.6	C_γ-H_γ in the structure of β-O-4(A)
$A_{\gamma'}$	63.0/3.8 ~ 4.10	C_γ-H_γ in the acetylated β-O-4(A) structure
B_α	85.4/4.6	C_α-H_α of β-β in resin alcohol (B)
B_β	53.5/3.07	C_β-H_β of β-β in resin alcohol (B)
B_γ	72.9/3.7	C_γ-H_γ of β-β in resin alcohol (B)
C_α	87.5/5.4	C_α-H_α in phenylcoumarin (C)
C_β	49.8/3.6	C_β-H_β in phenylcoumarin (C)
C_γ	62.9/3.6	C_γ-H_γ in phenylcoumarin (C)
D	60.6/4.0	Pinealcohol
G_2	112.6/6.8	C_2-H_2 in guaiacyl (G)
G_5	115.6/6.7	C_5-H_5 in guaiacyl (G)
G_6	121.1/6.5	C_6-H_6 in guaiacyl (G)
FA_2	110.3/7.2	C_2-H_2 in the structure of ferulic acid ester (p-FA)
FA_6	124.2/6.9	C_6-H_6 in the structure of ferulic acid ester (p-FA)
$PCE_{2,6}$	128.7/7.2	$C_{2,6}$-$H_{2,6}$ in the structure of p-coumaric acid esters
$H_{2,6}$	125.8/6.9	$C_{2,6}$-$H_{2,6}$ in the structure of *p*-hydroxyphenyl
X_5	62.8/3.3	C_5-H_5 in β-D-galactopyranoside

inside them, making them a strong skeleton structure. The reason why trees can stand tens of meters or even hundreds of meters is because of the adhesive force of lignin. Phenol is a traditional wood binder, and lignin has a similar structure to phenol. Replacing phenol with lignin can result in lower production cost and less environmental pollution. Therefore, it is a candidate to replace phenol in the preparation of more environmentally friendly and economical wood adhesives. Lignin based adhesives can be divided into two categories, that is, lignin-based formaldehyde resin and lignin-based formaldehyde free resin. The former group includes the most widely used types of binders such as lignin-phenol-formaldehyde, lignin-urea-formaldehyde, and lignin-melamine-formaldehyde resins. Although these binders have excellent water resistance, wear resistance, and adhesion, their increased cost and storage stability are limited. Lignin-based formaldehyde-free resins include lignin-polyurethane, lignin-furfural, lignin-polyamine, lignin-tannin, and lignin-soy protein. They have the advantages of abundance, environmental protection, and low cost. However, most of them have poor water resistance and are easy to mold.

Lignin sulfonated is used as a dispersant to disperse dyes. The solubility of disperse dyes in aqueous solution is very low. Adding dispersant is beneficial to prevent dye particles from caking and stabilize dye dispersion (Qin et al. 2015). Lignin sulfonated prevents particles from clumping together by introducing steric hindrance and static electricity between particles. Lignin dispersants are also used for kaolin dispersion, where they adsorb to the surface of particles and change the overall surface charge density of the suspension by inducing electrostatic or spatial repulsion between particles.

Lignin can be used as a surfactant, and its amphiphilicity is attributed to its aromatic core structure and the hydroxyl group on the polymer chain. The use of GA (acetallic acid)—lignin as a surfactant in the formulation of a cosmetic hand cream composed of industry-related ingredient—was investigated, maintaining the color or odor of the formulation. Ga-lignin is a biopolymer that can be extracted from lignocellulosic biomass in one step. As an effective surfactant, lignin does not need to be modified again, so it has a good prospect in the development of new bio-based surfactant products.

Because of its structure and properties, lignin has a good prospect in industrial applications. However, the lack of in-depth analysis on the structural properties of lignin modified products is one of the reasons for the limited application of lignin. At present, lignin-modified products have wide application prospects in industry due to their excellent properties. However, its performance, cost, and other factors cannot be compared with traditional chemical products. Further study on the modification mechanism of lignin and its application is of great significance for high value conversion and effective utilization of lignin.

13.5.2 Agricultural Applications

Lignin has good sustained-release and chelating properties and can be used as a fertilizer sustained-release carrier and coating material. Lignin-based slow-release fertilizers can be prepared by ammoxidation, Mannich reactions, and other chemical modifications, coating (with or without chemical modifications) and chelating modification. Lignin is an ideal carrier for new fertilizers such as compound fertilizer and phosphate fertilizer because of its slow degradation and nutrient release process. The slow-release lignin fertilizer prepared by modification of different elements has the advantages of strong biological activity, high stability, low pollution, and low cost. Besides, in the process of irrigation, ammonia oxidation of lignin nitrogen fertilizer, and lignosulfonate nitrogen fertilizer have the advantages of slower nutrient release and less leaching loss. Nutrients such as nitrogen can be slowly released by slow-release nitrogen for the crops to absorb and use. In this case, the frequency of fertilization is reduced, resulting in a much lower probability of water pollution from leached fertilizers. In addition, lignin has great development prospects due to its characteristics of inhibiting soil urease activity, reducing nutrient loss and improving nitrogen use efficiency (Ahmad et al. 2021).

Lignin can be obtained by combining it with diammonium phosphate and some auxiliaries at the right temperature to obtain an enhanced phosphate fertilizer. Lignin extracted from acidified black liquor contains hydroxyl, carboxyl, and other groups that can react with oxygen and chloride ions, thus reducing the fixation of phosphorus in soil. In addition, soil available phosphorus mainly comes from Ca-P, and modified lignin can improve the application effect of phosphorus fertilizer by increasing the contents of Fe-P and Ca-P in soil. For example, there were studies using sodium lignosulfonate to treat phosphor powder, to transform insoluble chemical bonds into soluble ones, so as to improve the content of active phosphorus and obtain enhanced phosphate fertilizer (Caoxing et al. 2018). In drainage crop systems, nitrogen from common urea is completely released, and this nitrogen is easily leached. In contrast, the nutrient release of modified lignin nitrogen fertilizer is relatively slow, which has the effect of anti-leaching. Urea is highly soluble in water, so the use of a physical barrier can slow the dissolution of urea and control its release. The modified lignin powder was uniformly coated in urea with adhesive and was repeatedly prepared into lignin-coated urea. Nitrogen release begins when water hits the acetylated lignosulfonate layer and penetrates the coating until it reaches the core. Soluble elements were then carried by the water into the soil along with nutrients (Sadeghi et al. 2017). In addition, the three-dimensional polymer network structure of lignin also plays an important role in promoting plant development (Zheng et al. 2020).

In pesticide application, lignin pesticide can reduce the risk of soil pesticide pollution and groundwater pollution caused by soil leaching. Lignin pesticides have the advantages of slow release, rich sources, and harmless chemical properties, and their derivatives are mainly used as dispersants and adhesives in pesticide applications. Bagasse lignin was oxidized and acetylated to obtain a biodegradable green fungicide with high thermal and optical stability (Yang et al. 2008). At the same time, all the ingredients of this insecticide come from the natural environment. They can degrade naturally and do not remain on agricultural products, thus protecting human health.

Lignin-based agricultural products have been shown to have better properties and are inexpensive compared to traditional agricultural chemicals, so these new agricultural chemicals are increasingly needed. Along with the call, lignin-based agricultural chemicals are a better and safer option. In addition, efficient recycling of agricultural biomass should be carried out for industrial large-scale production of lignin, so as to realize the sustainable development concept of “treating waste with waste and turning waste into treasure.”

13.5.3 Medical Applications

As a natural compound, lignins ecotoxicity can be easily solved. Because of the potential of lignin to enhance health, the promise of its medical use cannot be ignored (Figueiredo et al. 2018). These macromolecular compounds and lignin derivatives can be used to develop new drugs with different anti-inflammatory, heart protective, bone protective, neuro protective, and immune protective properties (Chowdhury 2014).

13.5.3.1 Lignin in Wound-Healing Dressings

The structure of lignin nanofibers is similar to that of extracellular matrix proteins. Lignin nanofiber gels were modified with arginine. Due to the healing effect of arginine, the resulting gels can promote wound healing, angiogenesis, epithelial cell regeneration, and collagen deposition (Reesi et al. 2018). Simultaneously, it was found that lignin could be used as an ion cross-linking agent of chitosan to obtain hydrogels with wound healing potential (Ravishankar et al. 2019).

13.5.3.2 Lignin in Diabetes Treatment

Studies have shown that modified lignin can inhibit α-amylase, nesting, and *Aspergillus flavus* (Barapatre et al. 2015). The study has demonstrated that these compounds have potential anti-hyperglycemic properties as a result of the restriction of glucose absorption after meals. A new hydrogen bond was formed between lignin and enzyme, which inhibited enzyme activity. In addition, through the condensation of lignin with epichlorohydrin oligomers and the amination reaction of the formed chlorine derivatives with polyamines, lignin adsorbents with hypolipidemia and hypoglycemia effects have been obtained (Spiridon 2020). They may be useful for patients with diabetic retinopathy because they help remove water and fat-soluble toxic metabolites from the serum.

13.5.3.3 Lignin-Based Material as Carrier and Delivery System

Because of its good biocompatibility, the biological carrier using Ginkgo lignin-carbohydrate as a raw material can be used for the culture of human hepatocytes (Houkuan et al. 2017). Sugarcane lignin can deliver methotrexate, a medicine used to treat rheumatoid arthritis (Wahba et al. 2015). Because lignin is well dispersed between capillaries, it can transport drugs to inflamed tissues. In addition, lignin copolymers have good DNA-binding ability and are non-cytotoxic, and sulfate lignin has been used to develop gene delivery materials.

13.5.3.4 Application of Lignin and Its Derivatives in Antiviral and Anticancer

Lignin and its derivatives have shown effective antiviral effects against HIV, HSV, influenza virus, and EMCV, but whether this inhibitory effect exists in other infectious microorganisms has not been clarified. Lignosulfonate (LA) is a polymer derived from lignin, which has antiviral activity against human immunodeficiency virus (HIV) and herpes simplex virus (HSV). LA sulfonate inactivates HIV by inhibiting the virus from attacking cells (Qiu et al. 2012).

Besides, lignin carbohydrate, which has been shown to reduce the incidence of breast tumors, is derived from bamboo (Huang et al. 2018). Immunological analysis showed that the drug inhibited the growth of breast tumor cells and stimulated macrophages immunologically. Sugar and structure play an important part, the polymeric structure of the lignin-carbohydrate complex leads to antiviral activity, and the high-order structure of polysaccharides and lignin can enhance immunity (Sakagami et al. 2005). Studies have shown that Fe_3O_4-lignin nanoparticles can be magnetized to saturation by magnetic field. This makes Fe_3O_4-lignin nanoparticles potentially useful in cancer treatment and diagnosis (Figueiredo et al. 2018). As a result, when magnetic fields are used, they act as a vehicle to transport pharmaceutical molecules to particular targets in the human body. At the meantime, the study found that lignin nanoparticles can be used as the carrier of poorly water-soluble medicine (benzoline and sorafenib) and also as the carrier of water-soluble anticancer drugs (capecitabine), which have inhibitory effects on different cancer cells.

Lignin and its derivatives, as multipurpose materials in the field of medicine, have broad application prospects. At present, most of the studies on lignin in the field of medicine are still at the theoretical level, and clinical trials are needed before the practical application. Clinical trials, however, are time-consuming and expensive. Therefore, before conducting clinical trials, there needs to be a full assessment of the feasibility of the research.

13.6 Conclusion and Prospect

In conclusion, in the pursuit of green renewable resources today, the extraction of lignin from agricultural waste and its exploitation and utilization have become a hot topic. Because of its complex structure, how to extract lignin efficiently and apply it to production and life is worth further study. At present, the characterization methods of lignin include NMR and HSQC NMR. Among them, the former has been frequently used as the preferred method to characterize the complex structure of lignin, and the latter also has an important position in the field of papermaking. Lignin has been widely used in industry and agriculture and has shown great potential in medicine. However, before conducting clinical trials, there needs to be a full assessment of the feasibility of the research.

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Rice Husk: From Agro-Industrial to Modern Applications

14

Shweta Mishra, Indramani Dhada, and Putul Haldar

Abstract

The concept of a circular bioeconomy is getting developed due to exhaustiveness of natural resources and exorbitant waste production. The use of valuable by-products assures to shore up and escalate environmental sustainability. Worldwide production of rice accounts for more than 750 million grain tons and 150 million husk tons annually. Rice husk contains valuable biomaterials, each of which has extensive applications in various fields (23–35% cellulose, 26–31% lignin, 18–21% hemicellulose, 15% pentosans, 16% minerals including silica). Although rice husk is a rich source of valuable and widely used materials, unfortunately it is still not widely used in the world. In this chapter, its industrial applications are mentioned to promote its use on a large scale. The proportions of each component depend primarily on rice genotype, soil chemistry, and climatic conditions. Rice husk (RH) and its derivatives, such as rice husk ash (RHA), rice husk biochar (RHB), rice husk hydrochar (RHH), and activated carbon (RHAC), have been placed forefront for applications in agriculture and other industries. While the investigation of RH's composition, microstructure, and by-products has been done intensively, owing to its unique characteristics, it is still an open-ended area with numerous scopes for research, particularly in identifying RH potential applications. Hence, disregarding the environmental effects, the production of value-added products and RH applications in various industries are in the spotlight. A comprehensive review of RHA, RHB, RHH, and RHAC obtainment and their applications in various fields (including fuel and other energy resources, construction materials (concrete and firebrick), pharmacy, medicinal uses, and nanobiotechnology) is the focus of this chapter.

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Keywords

Circular bioeconomy · Rice husk-activated carbon · 22 Rice husk ash · Rice husk biochar · Rice husk hydrochar

14.1 Introduction

A bio-based circular economy accelerates a sustainable future, tampering with the effects of environmental changes, including global warming. Biomass recycling leads to the economy boosting and promises better use for agricultural wastes (Muscat et al. 2021). As per the reports, in 2021, the size of Global Rice Husk market was estimated at USD 525.78 million, and it is further being projected to reach USD 860.17 million in the next 7–8 years, exhibiting a CAGR of 7.29% during the forecast period. Rice husk (RH, Fig. 14.1a), seed protectant layer that hinders germination (Kim et al. 2012), is one of the primary agricultural wastes produced in rice-producing countries. Though it has many uses, it is not broadly used economically. RH accounts for approximately 20% of rice weight (Kumar et al. 2013). This high amount of RH poses risks to the environment. RH is mainly made up of cellulose (25–33%), lignin (25–31%), and hemicellulose (18–21%) with lower amounts of pentosans (15%) and minerals, including silica (16%) (Fig. 14.1a). Transpiration of organic matters and proteins present in the cell wall generates amorphous silica in rice (Guerriero et al. 2016). The quantities of each RH constituent are dependent on rice genotype, soil chemistry, and climatic conditions (Ugwu et al. 2019). RH is produced in the rice paddy grain shelling and milling process (Fig. 14.1b) to produce white and polished rice with no husk and bran (Prabhakaran et al. 2017). Following harvest, rice dries, and the paddies are ground and peeled.

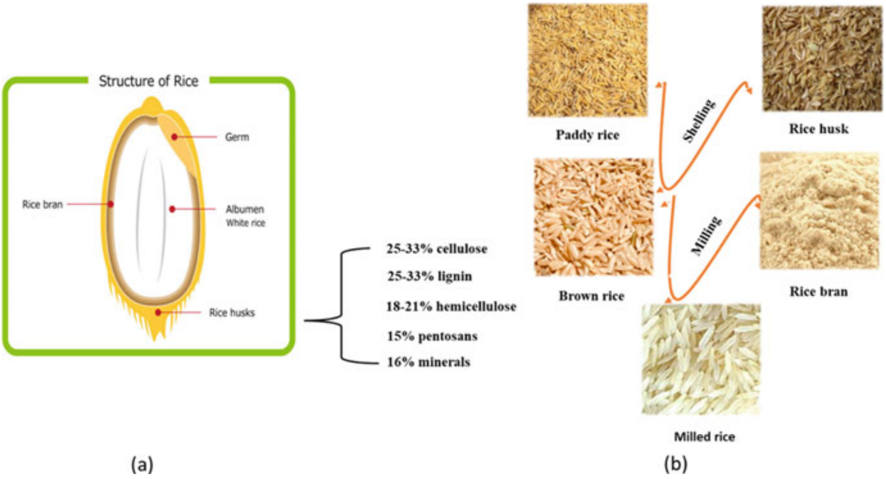

Fig. 14.1 Rice grain constituents and grain processing

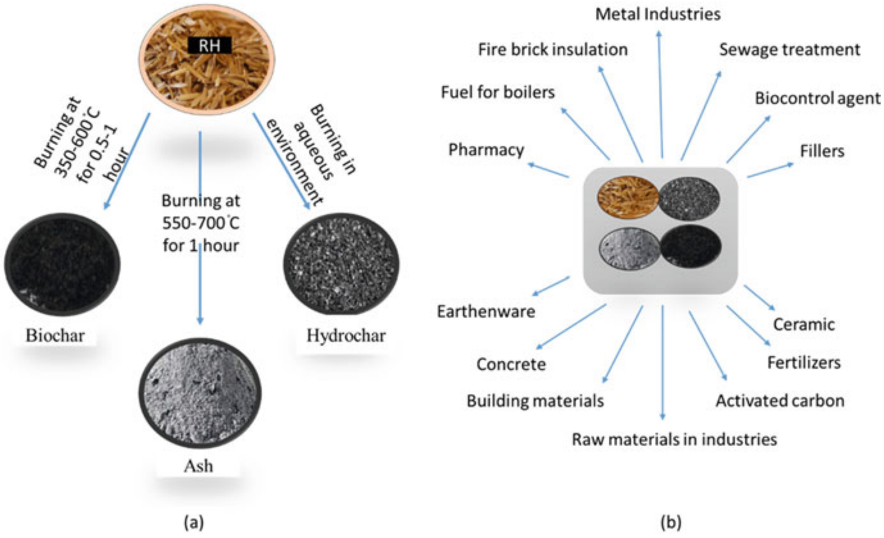

Fig. 14.2 RH, its derivatives, and application

Rice milling process is done in two ways, that is, traditional and mechanical methods—with mortar and pestle or hand stone in the traditional method (Dhankhar 2014) and the use of different industrial mill types (Huller, Sheller-Huller, Sheller-Cone Polisher) in the mechanical method (Dhankhar 2014). To produce ash (RHA), biochar (RHB), hydrochar (RHH), and activated carbon RH are further processed.

RH can be used as the bed and energy source in solid-state fermentation, an environment with very little water (Cruz Quiroz et al. 2014), to produce microorganisms for agro-industrial applications (Nighojkar et al. 2019) (Fig. 14.2). It is also being used as fuel for boilers, steam and electricity generation, paper and board production, and animal feed (Kalderis et al. 2008). In broiler farms, RH is being used as a substrate (Chaitanoo et al. 2021). RH can remove all kinds of dyes, organic or inorganic pollutants such as metal ions, phenols, pesticides, and atmosphere contaminants; hence, it has applications in environmental sustainability (Chen et al. 2011). RHA is produced via burning in order to produce silica (Putranto et al. 2021). Amorphous silica is a good alternative to ordinary silica (obtained from quartz). It can be used to produce ceramic materials, refractory, glass, and silica aerogel composites (Hossain et al. 2018) (Fig. 14.2). Masks made from silver nanocluster + silica are also manufactured from silica obtained from RH. Such masks are capable of efficiently reducing SARS-Cov-2 infection to zero (Prabha et al. 2020). Burning of RH under limited oxygen conditions at relatively low temperatures leads to production of RHB (<700 °C; Fig. 14.2) (Zhang et al. 2020a). Application of RHB has been shown to increase the bioavailability of soil nutrients, decrease in N_2O release and greater nitrogen uptake, and reduction of soil surface bulk density in agronomy (Tan et al. 2018). RHB causes medium soil acidity, and the uptake of heavy metals such as Ba, As, Pb, Cu, and Zn by crop can be successful (Campos et al. 2021). For example, KOH-enhanced RHB produced at 300 °C has an excellent stabilizing effect on Cd and Pb (Wang et al. 2020). In the apple orchard, applying a mixture of RHB and organic fertilizer showed an improved soil organic carbon content and bacterial diversity (Duan et al. 2021).

RHH is being generated at lower temperatures between 180 °C and 350 °C in an aqueous environment (Li et al. 2019a, 2021) and longer storage times (2–16 h) in comparison to biochar (Fig. 14.2; Kalderis et al. 2014; Nizamuddin et al. 2019). RHH can show promising effects on fuel cells, soil fertility improvement, and immobilization of soil heavy metal cations and anions (Nizamuddin et al. 2018). For instance, nitrogen pollution runoffs can be diminished by a bioretention column filled with $FeCl_3$-modified RHH (Smith et al. 2020; Wang et al. 2021). RHH can also be used as an adsorbent although it is poor in adsorbing nonpolar organic matter and has less stability (Nizamuddin et al. 2019). Polymer composites produced by use of RHB and RHH as fillers have recently received much attention, particularly in environmental, both aquatic, and atmospheric pollutant remediation (Nizamuddin et al. 2019; Zhang et al. 2020a). Two-step procedure, that is, carbonization and activation can be used to obtain activated carbon/charcoal (AC) (Cheenmatchaya and Kungwankunakorn 2014). In the carbonization process, raw carbonaceous materials such as RH are carbonized for 1 h at 200 °C–400 °C in an inert muffle furnace to produce charcoal. The produced material is generally activated chemically by H_3PO_4 (Cheenmatchaya and Kungwankunakorn 2014). In pyrolysis process, the thermochemical decomposition of organic matter such as RH into non-condensable gases, condensable liquids, and solid residues has also been used in RHAC production (Zhang et al. 2019). RHAC is an economic adsorbent in environmental protection, water, sewage treatment, and gas filters (Chen et al. 2011). The capacity of carbon adsorption depends on the raw material, penetration rate, and treatment conditions such as pyrolysis temperature and activation time (Crini 2006). RHAC has a high conductivity potential to be prepared as a double layer and, hence, can be used as electrode materials to produce electric double layer capacitors (Chen et al. 2011). RH and its ingredients (such as silica) or derivatives are used in various industries and agriculture (Fig. 14.2). The literature published on RH applications and prospects are summarized in Table 14.1.

14.2 Applications of RH in Agricultural Industry

14.2.1 Biocontrol Agents

Use of biocontrol agents is increasing over chemical pesticides due to many health and environmental side effects. Cheap substrates are now getting explored to produce these agents. Fungal entomopathogens are a method of choice to suppress most pests and their larvae (Lacey et al. 2015). *Beauveria bassiana* and *Trichoderma harzianum* are fungal biopesticides that can be produced on solid-state fermentation (SSF) setup containing RH (Sala et al. 2020, 2021). Likewise, a porous terracotta disc (PTD) was made containing RH nanoparticles (AgNPs-RH) to control insect

Table 14.1 Applications of RH and its derivatives

Applications	Sources	Remarks
Agriculture industry	Lacey et al. (2015)	Fungal entomopathogens
	Sundaramahalingam et al. (2020)	Porous terracotta disc (PTD)
	Nair and Sawant (2006)	As biocarriers for commercial formulation of pesticides
Soil fertilization and soil improvement	Thiyageshwari et al. (2018)	Composting
	Ismail and Mokhtar (2020)	Used in removal of estrone, β-estradiol, estriol, and antibiotics present in manure
	Zhang et al. (2021)	Microbial degradation of manure and prevents nitrogen loss
	Thiyageshwari et al. (2018)	Agricultural productivity enhancement and lessen chemical inputs
	Shak et al. (2014)	Vermicompost
	Tsegaye and Tefera (2017)	Transformation of inedible biomass residues into nutritional proteins
	Iruoma and Nduka (2013)	Commercial mushroom production enhancement
	Abou El-Magd et al. (2006)	Development of soil microbiota
Food and feed industry	Ansari et al. (2021)	Aflatoxins, carcinogenic metabolites production
	Li et al. (2020)	Food contaminant removal from edible oil
	Abazari et al. (2016)	Beneficial effects as insoluble fibers for developing gut microbiota
	Mopoung et al. (2020)	Helps in oxygen transfer in water
	Niu et al. (2022)	Reduces cd availability and ensure safe food production
	Firdus et al. (2020)	For fish feeding
	Melendez-Rodriguez et al. (2019)	Used in food packaging
Environmental applications	Shamsollahi and Partovinia (2019)	As environmental absorbent for removing pollutants
	Shuib et al. (2016)	Used for bioremediation purposes
	Li et al. (2019b)	Phytoremediation
	Chockalingam and Subramanian (2006)	As good adsorbent for removing copper, iron, and zinc from soil
	Yavari et al. (2018)	Contaminated soil improvement with herbicides
	Sadeghi Afjeh et al. (2019)	Removal nitrate ions from water as bio sorbent
	Swarnalakshmi et al. (2018)	Acid Orange 7, Amoxicillin, Metformin, and Carbamazepine contaminant removals

(continued)

Table 14.1 (continued)

Applications	Sources	Remarks
	Perez-Marin et al. (2008)	Removal of heavy metals from industrial wastewaters
	Soltani et al. (2015), Bernardo et al. (2017) and Wang et al. (2018)	Production of activated carbon, syngas, silica, and biofuel
Construction materials	Danewalia et al. (2016)	Synthesis of cement mortar and glass-ceramics
	Ataie (2021)	Production of Portland cement type with greater mechanical strength
	Nath Bhowmik and Pal (2022)	Production of cement grouts with greater potential of hydration and workability
	Kumar et al. (2022)	Production of lighter and strong bricks than clay bricks
Pharmacy and medicine	Ogaji et al. (2012)	Availability of fillers saves pharmaceutical costs and ease of use in drug production
	Jesudoss et al. (2018)	Production zeolite (aluminosilicate), which has lung anticancer properties
	Edrisi et al. (2018)	Help obese individuals to reduce their appetite
	Prabha et al. (2020)	Used for biosensors, bioimaging, drug delivery, and manufacturing of SARS-Cov-2 anti-mask
Nanobiotechnology	Daulay et al. (2022)	Production of pure silica and nano-silicon, used for production of lithium-ion batteries
	Motaung and Luyt (2010), Morpurgo et al. (2010), Pode (2016) and Bakaev and Pantano (2009)	Production of nano silica with applications in fillers, pharmaceuticals, catalysts, and chroma-topography
	Duc Pham et al. (2020)	Effective in removal of antibiotics

larvae efficiently (Sundaramahalingam et al. 2020). In another study, the antibacterial activity of RH covered with silver nanoparticles indicated twice the activity of the time that particles were used alone. This stronger behavior was related to higher adsorption of RH and its potential for slow release of silver ions (Cui et al. 2015). RH is used as bio-carriers in the commercial formulation of pesticides for more excellent dispersion, solubility, and wettability (Nair and Sawant 2006).

14.2.2 Soil Fertility Improvement

Bioavailability of silica in rice paddy fields, which affects crop growth and development, and hence proper processing of RH can be beneficial to soil (Badar and Qureshi 2014). RH can be used in composting (Thiyageshwari et al. 2018). For instance, the combination of RH compost + RHB + mycorrhiza 136 on *Echium amoenum* has a remediation effect on removing added antibiotic sulfadiazine from greenhouse soil (Ahmadabadi et al. 2019). RHB + *Bacillus pumilus* application has indicated their effect on rice productivity genotype-dependent manner (Win et al. 2019). The use of RHB and RHAC on bacterial cultures has indicated positive impact on the growth, sporulation, and antifungal activity of *Bacillus* sp. (Ebe et al. 2019). RH can also be used as an absorbent in removing the harmful substances such as estrone, β-estradiol, estriol, and antibiotics present in manure that, by law, should not be in the fertilizer (Ismail and Mokhtar 2020). Inappropriate use of poultry fertilizer is accompanied by a significant release of NH_3, heavy metals, and estrogen. RHB helps in microbial degradation of manure and prevents nitrogen loss, reducing the bioavailability of heavy metals and hormones (Zhang et al. 2021). RHB can improve rice resilience to drought when used in 3 t/ha. Soils generally have less content of organic matter. In a sustainable agricultural system, biofertilizers are cost-effective, environmentally friendly, and a renewable source of nutrients (Maki et al. 2012). RHB is also capable of reducing the need of agrochemicals like fertilizers. Composted RH can be returned to the soil to protect and improve soil organic matter, increase agricultural productivity, and lessen chemical inputs (Thiyageshwari et al. 2018). Worms use RH and rice residual to produce vermicompost (Shak et al. 2014). In combination with organic and mineral fertilizers, RH and RHB have also been used as microbial carriers, effective in soil improvement, microbial diversity, and nitrogen uptake by a plant (Tan et al. 2018; Duan et al. 2021).

14.2.3 Mushroom Production

Crop residue management has a suitable bioconversion process of Mushroom cultivation. Saprophytic fungi develop naturally in rotten wood on tree trunks, decaying organic matter, and soil rich in moist organic matter (Tsegaye and Tefera 2017). Mushroom cultivation with agricultural residues is a technique of environmental protection. The transformation of inedible biomass residues into nutritional proteins in the form of fungi is of great importance (Tsegaye and Tefera 2017). Casings of sawdust and RH can be used as substrates to provide moisture and proper conditions for the initial growth, improve quality and increase yield for commercial mushroom production (Iruoma and Nduka 2013). For instance, Pleurotus pulmonarius is an edible fungus that grows on agricultural waste (Iruoma and Nduka 2013).

14.2.4 Mulching

Mulch is a spreadable material applied in the soil in order to reduce water evaporation, prevent soil erosion, slow down the release of nitrogen for plant uptake, inhibit weed growth, and improve the biological (soil microbiota), physical, and chemical properties of the soil to increase productivity (Nwokwu and Aniekwe 2014). Assume that RH is used as mulch alone or in combination with sawdust or paddy straw, then it can maintain soil moisture and temperature, preserve soil organic matter, improve soil structure, and eventually generate a proper microenvironment for the development of soil microbiota (Abou El-Magd et al. 2006).

14.3 Applications in Food and Feed Industry

Aspergillus produces aflatoxins, carcinogenic metabolites that enter the food chain (Ansari et al. 2021). RH has shown promising absorptive function toward aflatoxins (Scaglioni and Badiale-Furlong 2016). Further studies showed the potential of magnetic mesoporous silica from RH in removing this food contaminant from edible oil (Li et al. 2020). RH is a good substitute for costly peanut protein for rabbit diets as a source of fiber and has anti-aflatoxin properties with high economic efficiency (Adeniji et al. 2014). RH has low nutritional value due to its constituents, including silica and lignin, and is not suitable for ruminant feed (Abazari et al. 2016). Also, it has beneficial effects as insoluble fibers for developing gut microbiota and to be used as bulk feeder in poultries and broiler farms (Abazari et al. 2016). Adequate use of RHB has been reported in aquaponic (hydroponic + aquaculture) for water treatment, increased oxygen transfer in water, and higher growth rate of fish and plants (Mopoung et al. 2020). RHAC is also used in fish (trevally giant; *Caranx ignobilis*) feeding with a significant effect on the daily and absolute growth rate (Firdus et al. 2020). Rice husk biochar has capability to reduce Cd availability and ensure safe food production (Niu et al. 2022).

14.4 Applications in Environment Development

Development in environment-friendly and sustainable materials that promote wastes to be reused has a significant bearing on the economy (Samaddar et al. 2018). Crop residues are one of the biggest global sources of biomass that remained neglected up to years and often discarded or burned for energy recovery eventually causing threat to the environment (Duque et al. 2019). RH is a good environmental absorbent for removing pollutants, including xenobiotics coming from the industrial zones, contaminating soil and water (Shamsollahi and Partovinia 2019).

14.4.1 Remediation of Soil

Surface soils carry heavy metals or become contaminated by industrial effluents, air pollution, and/or pesticide drift from adjoining farms. Environmental pollution through metals affects the fertility of agricultural soil, reduces crop yielding, and affects the human food chain (Wei and Yang 2010). RH does not decompose easily due to high lignin and cellulose present in, so it could not be effective to directly apply RH in soil (Rosa et al. 2012). Carbonization of RH produces charcoal and vinegar in the absence of oxygen. RH charcoal increases the concentration of calcium, magnesium, potassium, and silicon in soil as well as soil pH. Long-term use of RH charcoal has indicated beneficial effects on soil fertility (Chien et al. 2011; Phuong et al. 2019, 2020). RH has been used as a fungal growth enhancer (*Marasmius cladophyllus*) that is being used for bioremediation purposes (Shuib et al. 2016). RH and RHB in combination with *M. circinelloides* and soybean were used for phytoremediation (Li et al. 2019b). Soil contamination with lead, a nondegradable and carcinogenic metal, is a serious global concern with negative impacts on healthy crop production (Laidlaw et al. 2017). RH is a good adsorbent for removing copper, iron, and zinc from soil (Chockalingam and Subramanian 2006). RHB and RHA can improve metal-contaminated soil properties (Wallheimer 2012; Kiran and Prasad 2019) and increase plant growth parameters via better nutrient intake and antioxidant enzymatic activities. Soil applications of RHA have been shown to reduce lead concentration in *Ricinus communis* roots by 87% compared to control plants (Kiran and Prasad 2019). Immobilization and removal of contamination by heavy metals from soil have been shown to achieve by RHB alone (Derakhshan-Nejad and Jung 2019; Wang et al. 2019), surface-modified RHB by iron oxide (Cope et al. 2014), sulfur-modified RHB (O'Connor et al. 2018), RHB + Zeolite (Zheng et al. 2020), and KOH-treated RHB (Wang et al. 2020). Soil chromium contamination is an important environmental issue. Use of zerovalent iron nanoscale (NZVI) 225 supported by RHB as a modifier managed to minimize Cr contamination in soil (Liu et al. 2019). Use of RHB can lead to soil carbon sequestration. RHB bioremediation effect in heavy metal immobilization in soil is shown to be dependent on its production condition. Shi et al. (2019) showed that RHB produced at higher temperatures (500 and 700 °C) has less functional groups and greater remediation activity. Furthermore, RHB has shown to be effective in adsorbing water contaminations in oil (Kandanelli et al. 2018). β-cyclodextrin-functionalized RH has shown to act as remediator in heavy metals and organic pollutants such as pesticides in a pH dependent/independent manner (Qu et al. 2020). RH has also been used as a carrier for the herbicide 2,4-dichlorophenoxyacetic acid and has been shown that RH can lead to herbicide diffusion (Abigail et al. 2016). Biochar made from RH and palm oil empty fruit bunch was shown to be able to improve soil contaminated with herbicides (Yavari et al. 2018). In another study, it was shown that the use of RHA in combination with cow dung can remove glyphosate, a widely applied herbicide, from water (Garba et al. 2019). RHA and RHB have also been used in the absorbance of other herbicides/pesticides and other chemicals such as paraquat, 2–4-D, 4-chloro-2-

methylphenoxyacetic acid, metolachlor, atrazine, imidacloprid, and fenoxaprop-ethyl (Rongchapo et al. 2013; Wei et al. 2017).

14.4.2 Water Treatment Industry

Effluents from various industries such as agriculture, leather, cosmetics, textiles, pharmacy, and food contain unwanted biological and chemical compounds, and they get disposed-off in open seas, endangering aquatic life (Swarnalakshmi et al. 2018). The most dangerous chemicals entering the water are antibiotics, painkillers, and hormonal drugs (Balarak et al. 2020). They enter the water through the sewage system of drug factories, households, and hospitals (Balarak et al. 2016). Antibiotics sustain in the aquatic and terrestrial environment in their original form, which has come out as an environmental problem in recent years (Balarak and Mostafapour 2019). RH modified by 3-amino-propyl triethoxysilane was shown to be able to remove scandium from wastewater (Salman et al. 2020). Betiha et al. (2020) demonstrated that mesoporous silica-polymer hybrid produced from RH and polyvinylpyrrolidone absorbs divalent heavy metals from wastewater. RHB is effective in removing antibiotics like levofloxacin and tetracycline from aqueous solutions (Yi et al. 2016; Bushra and Remya 2020). Nitrate water pollution is a major problem. Purification of nitrate from water by biosorption is a way forward for nitrate removal (Zhang et al. 2020c). RH has been used to remove nitrate ions from water as bio-sorbent (Sadeghi Afjeh et al. 2019). As an effective drug absorbent, RHA has also been used for Acid Orange 7, Amoxicillin, Metformin, and Carbamazepine contaminant removals (Swarnalakshmi et al. 2018). Standard methods of removing heavy metals from industrial wastewaters are reverse osmosis, electromechanical reduction, ion exchange, chemical precipitation, and membrane filtration, which are very expensive (Perez-Marin et al. 2008). The absorption capacity of agricultural wastes due to high porosity and consequent large surface area for heavy metals is significantly high (Nguyen et al. 2013).

14.4.3 Removal of Dye

RHB and activated charcoal are capable of adsorbing and removing chemicals from industrial effluents (Prapagdee et al. 2016). Some dye variants are very toxic and have mutagenic and disease causative agents and need to be removed from the environment (Chowdhury et al. 2011). Dye removal procedures include biological oxidation, chemical deposition, and adsorption of dyes with adsorbents (Vadivelan and Kumar 2005). RH and RHB were used to remove color compounds (Vaz et al. 2017).

14.4.4 Fuel

Energy demand is rapidly increasing globally, and a growth of about 30% by 2040 is projected (OECD 2016). Accordingly, considerable efforts are being made to substitute fossil fuels with more sustainable renewable energy sources such as agricultural waste (Ge et al. 2016). Rice husk has a three-dimensional net structure of organic carbon and silica that is being used to produce activated carbon, syngas, silica, and biofuel (Soltani et al. 2015; Wang et al. 2018). However, RH can be used as coal replacement with lesser pollutants (Nayak et al. 2017). Biogas is generated by anaerobic digestion of organic matter by bacteria, which in the process of digestion produces both energy (gas) and valuable soil products (liquid and solid). Biogas contains 50–70% methane, 30–40% carbon dioxide, and small amounts of other gases (Xu and Li 2017).

Green hydrogen is a hydrogen produced from water using renewable energy sources (Ota et al. 2014). RH has been used to produce green biohydrogen (Lat Reano 2020). RH is also being used as the second-generation fermentative resource in bioethanol production because it delivers fermentable sugars such as glucose, arabinose, xylose, galactose, and mannose (Kaur and Singh 2017; Tabata et al. 2017). RH is a good raw material in power plants, as it performs better than fossil fuels considering environmental emissions (Chungsangunsit et al. 2005). RH gasification produces syngas that has become a topic of interest in recent years (Bernardo et al. 2017).

14.4.5 Other Energy Resources

Nanostructures of rice shells can be used in modern energy fields, that is, Li-ion batteries, solar cells, supercapacitors, and triboelectric nanogenerators (Wang et al. 2018). RH can be used to produce cheap carbon, used for Li-ion batteries (Zhang et al. 2020b). RH SiO_2 can be converted to high-pure Si with use in uniform nanoporous silicon nanostructures with excellent performance as Li-ion battery anodes (Cho et al. 2016). RH is also being used to make carbonaceous materials such as graphene oxide used in electronics, biomaterials, energy generation, and environmental remediation (Manpetch et al. 2022). RHA can be used to produce a cheap and more environment-friendly source of silicon that can be used in solar cells (Putranto et al. 2021).

14.5 Applications in Construction Materials

14.5.1 Ceramics Production

Ceramics are produced by RH and RHA. For instance, a porous ceramic was made from a composite of alumina + RHA (Ali et al. 2017). The procedure for producing ceramics using RH is as follows: milling, combining in a ratio of 3:1 of RH with

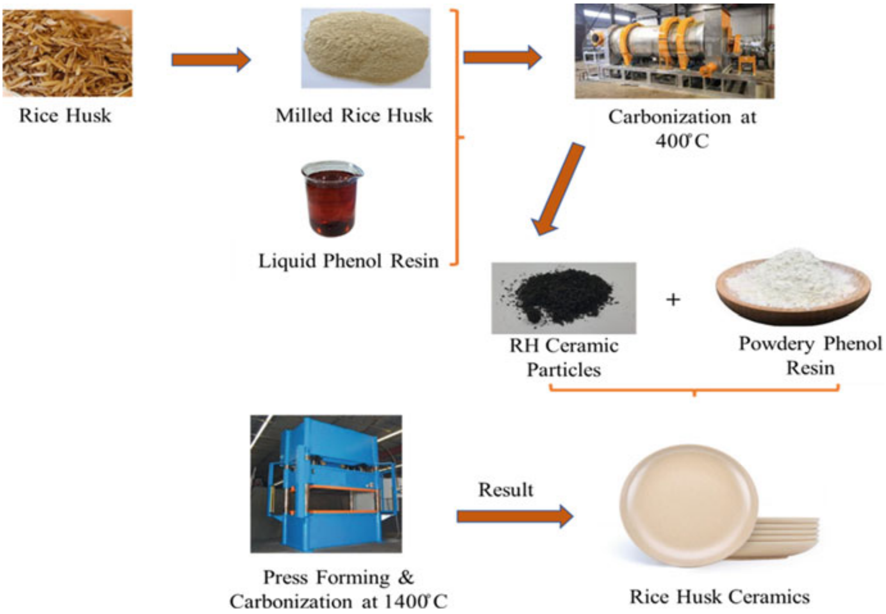

Fig. 14.3 Steps in ceramic production from RH

liquid phenol resin, drying at 150–180 °C, carbonization, crushing carbonized mixture, pressing the crushed mixture with powdery phenol resin to make a disc, re-carbonization of discs, and finally cooling of ceramic discs (Shibata et al. 2014; Fig. 14.3). In the ceramics industry, silica (SiO_2) is the backbone (Carter and Norton 2013); manufacturers use silica sand, gravel, sandstone, granite, quartz, and quartzite as the source of silica. RH is rich in silica that can be used in the ceramic industry, letting natural resources remain safe and sound (Hossain et al. 2018). RHA has been used for the synthesis of cement mortar (Chatveera and Lertwattanaruk 2014) and glass-ceramics (Danewalia et al. 2016). RH has also been used in synthesis of MCM-22 zeolite with application in adsorption and catalysis (Cheng et al. 2012), silicate-phosphate glasses (Kaur et al. 2020), and biosilicate ceramics (Choudhary et al. 2021).

14.5.2 Concrete Production

Recycled aggregate concrete (RAC: aggregates from recycling clean concrete waste with little other building waste (Marinkovic and Carevic 2019)) has started to be used instead of natural aggregate concrete (NAC: concretes obtained from natural aggregates extracted from nature (Yuan et al. 2021)) due to a bigger attention toward environment preservation and economical sustainability (Qureshi et al. 2020). However, RAC is less durable compared to NAC due to its high porosity (Qureshi et al. 2020). Durability of RAC can be enhanced by the additives of different kinds including RHA (Hu et al. 2020; Qureshi et al. 2020). Addition of RHA in on-shore structures help cement to improve its durability, avoid cracks, and improve its anti-fouling properties, and it can also be considered as green self-consolidating concrete (Lertwattanaruk and Makul 2021). RHA (5%) + sugarcane bagasse ash (5%) + cement (90%) has shown to produce better concretes (Channa et al. 2021). Portland cement is produced by the mixture of alkaline solutions (activator) such as NaOH and aluminosilicate materials (slag) (Awoyera and Adesina 2019). RHA can be used as sodium silicate in alkali-activated slag to help in cementing and production of a Portland cement type with greater mechanical strength (Ataie 2021). RHA (15%) + polypropylene (0.25%) + cement (84.75%) showed to result in a reinforced concrete (Memon et al. 2021). RH have large amounts of silica nanoparticles on its surface that makes it suitable to produce cement grouts with greater potential of hydration and workability hence used as slurry additive (Nath Bhowmik and Pal 2022). Application of RHA nanoparticles (3%) in cement indicated its potential in forming ultra-high-performance concrete (UHPC) with the highest compressive strength compared to a concrete made from a chemical nano-silica (Mostafa et al. 2020).

14.5.3 Brick Industry

The use of agricultural waste such as RH and bagasse ash next to used cement in the production of bricks has significantly reduced corresponding expenses. In addition to this, the produced bricks were lighter and more resistant than the clay bricks (Kumar et al. 2022). Insulating firebrick (IFB), bricks with low thermal conductivity and temperature resistance made of porous kaolin are being made by mixing organic matter with clay and then burning to create pores (Ugheoke et al. 2006). To produce porous IFB, RH is a good combustible material (Samuel 2015; Hossain et al. 2021). Rice husk ash is used to produce construction products such as cement and bricks (Jittin et al. 2020). It has been shown that a mixture of kaolin rice clay-plastic clay (4: 1:2) provides good insulation and a good refractory surface with optimal performance (Ugheoke et al. 2006).

14.6 Applications in Pharmacy and Medicine

Drugs are formulated with the help of additives in appropriate doses (Ugwu et al. 2019). Availability of fillers, used as a disintegrant, binder, gelling agent, lubricant, flavoring, emulsifier, suspending agent, bulking agent, and sweetener, saves pharmaceutical costs and ease of use in drug production (Ogaji et al. 2012). Biopolymers such as cellulose can be excipients, and cellulose obtained from RH can be used in this regard (Uwaezuoke et al. 2014; Kumar et al. 2018; Ugwu et al. 2019). Aerosil 200 V, a famous additive in numerous drug formulations, can be effectively replaced by SiO_2 obtained from RH (Ledesma et al. 2015; Salazar-Hernández et al. 2017). In addition to being used to formulate tablets, silicon dioxide (SiO_2) from RH is also used to thicken gels and manufacture photovoltaic cells and thixotropic agents (Rowe et al. 2009). Furthermore, RH contains xylo-oligosaccharides, which are helpful as a prebiotic for the growth and activity of intestinal microbiota with proven ameliorative effects on many diseases, including insulin resistance and diabetes (Khat-Udomkiri et al. 2019). RH contains phenolics and flavonoids that promote health and well-being (Lourith and Kanlayavattanakul 2013). RH can also help obese individuals to reduce their appetite (Edrisi et al. 2018). RH liquid smoke has been shown to ameliorate periodontitis by reducing inflammation (Budhy et al. 2021). RHA can be used to produce zeolite (aluminosilicate), which has been shown to have lung anticancer properties (Jesudoss et al. 2018). In the diabetic rat model, RH was used as a prebiotic to control blood sugar via preserving the intestinal microbiome (Khat-udomkiri et al. 2019). The preventive effect of purple RH extract on enzyme induction activity in murine hepatoma cells was reported; it has been shown to have a potent cancer chemopreventive activity in rat liver micronucleus (Chariyakornkul et al. 2019). RHA has some other applications in producing bioactive glass that can be used as bone regeneration material (Wu et al. 2009) and scaffolds in implant materials (Kaur et al. 2020). Similarly, silica-metal phosphate nanocomposites using RH with excellent biocompatibility with human mesenchymal stem cells can be used in bone tissue engineering (Athinarayanan et al. 2014). Homogeneous silica nanoparticles from RH have been used in biosensors, bioimaging, drug delivery, and manufacturing of SARS-Cov-2 anti-mask (Prabha et al. 2020). In recent times, agricultural waste processing such as RHA has been used as a biomaterial in biocompatible products. For example, RHA can be used to produce wollastonite, which is used for bone repair, implants, and tissue regeneration (Ismail and Mohamad 2021). RH, an inexpensive source of amorphous silica to produce silicon-based materials, is an environmentally friendly and low-cost waste source for commercial silica precursors (Shen 2017). RH-based biogenic silica-metal phosphate nanocomposites can be used in bone tissue engineering (Athinarayanan et al. 2014). RH flour has been used to produce poly(3-hydroxybutyrate) composite with application in food packaging (Melendez-Rodriguez et al. 2019).

14.7 Nanobiotechnology Applications of RH

The conversion of quartz sand and sodium carbonate to silica in industries is an energy-dependent methods (Affandi et al. 2009). Rice husk can be used to produce pure silica. RHA can be used to produce nano silica with applications in fillers (Motaung and Luyt 2010), pharmaceuticals (Morpurgo et al. 2010), catalysts (Pode 2016), and chroma-topography (Bakaev and Pantano 2009) through thermal and chemical processes (Ruey Ong et al. 2020). Burning RHA at temperatures between 500 °C and 700 °C leads to the production of amorphous nano-silica, whereas temperatures above 900 °C form the crystal structures of nano-silica (Chandrasekhar et al. 2006). RHA nano-silica is used as an effective biocompatible carrier for drug delivery, including the delayed release of antibiotics (Salavati-niasari et al. 2013) and anticancer drugs such as Doxorubicin (Porrang et al. 2021). RH has been used as a reducing agent in the production of silver nanoparticles with antibacterial activities (Suwan et al. 2018; Zhang et al. 2021). RH nano-silica was tested on cancer cell lines and fibroblast cell lines, which indicated more significant toxicity at first and little toxicity later on (Dhinasekaran et al. 2020). RH nano-silicon is used to prepare lithium-ion batteries (Daulay et al. 2022). Nanostructured mesoporous materials produced from RH and surface-modified by Fe were tested as photocatalytic degradation agents for the removal of various endocrine-disrupting chemicals (EDCs), such as herbicides (atrazine), and compounds derived from the plastic industry (bisphenol A) and the pharmaceutical industry (acetaminophen) (Carraro et al. 2020). RH nano-silica surface-modified by poly diallyl dimethyl ammonium chloride polyelectrolyte (PDADMAC) has adsorbing potential as demonstrated by the removal of antibiotics from an aqueous solution (Duc Pham et al. 2018). RH nano-zeolite has indicated waste water cleansing potential in removing paints from contaminated waters (Oviedo et al. 2021). Surface-modified nano-silica with protein (Pro MNS) is very effective in removing antibiotics such as ciprofloxacin as an environmentally friendly adsorbent (Duc Pham et al. 2020).

14.8 Economic Impact

The applications and importance of rice RH in different fields discussed above make it of great economic importance in various fields. Therefore, finding sustainable solutions for using RH in rice producing countries is necessary. For instance, with broad applications in various forms, RHA minimizes greenhouse gases by up to 1005 kg CO_2 eq/t product, drops costs by up to 8000 THB/t product, and creates jobs of five person-year/M THB (Prasara-A and Gheewala 2016). RHA gives the possibility of conventional product replacement (Balo 2015). For instance, in Nigeria, as RH was used for electricity generation in order to produce clean and cheap energy, it displayed to be economically sound with a net present value (NPV) of $1.68 million and a levelled cost of electricity (LCOE) of $0.07–0.11 kWh^{-1} (Salisu et al. 2021). In a similar study in Thailand, where rice is considered a staple food and RH is used as an alternative energy source, with numerous built-in power plants, more than six million tons of RH (70% of the total RH produced) are burnt each year (Energy Regulatory Commission 2015; Prasara-A and Gheewala 2016).

14.9 Concluding Remarks and Prospects

The cost of agricultural waste disposal can be reduced with the direct use of rice husk (RH) or its derivatives; on the other hand, it produces valuable compounds or even materials for components or devices such as solar cells and Li-ion batteries. Various applications have been reported for the RH derivatives, especially, rice husk ash (RHA), rice husk biochar (RHB), rice husk hydrochar (RHH), and rice husk-activated carbon (RHAC). This chapter indicates the wide applications of RH in various areas, including the agricultural industry, the construction industry, the fuel industry, the environmental sector, modern energy sector, the pharmaceutical industry, and medicine, in nanotechnology and biotechnology. For instance, RH has numerous medicinal applications because of high silica content and can be used for remediation directly. Recently, silica nanoparticles, which are obtained from RH, are used to produce protection masks against Covid-19. Nowadays, rice husk usage as raw material is playing a pivotal role in the bioeconomy via the entrance into the agricultural industry. Effective use of RH will help in increasing farm productivity and rural development. The fast growth of volume of scientific and technological publications on RH accounts for the constant evolution of its use from high-tonnage conventional to more specialized and advanced small-amount applications, expecting broader prospects in other fields in the upcoming years. The latter applications include the semiconductors and nanotechnology industries, two of the most influential drivers in today's society. Therefore, the economic impact of RH will influence not only the rice-producing countries but also those where it will be consumed as a value-added product.

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Production and Application of Nanomaterials from Agricultural Waste

15

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Abstract

This chapter focuses on the mechanisms of synthesizing nanomaterials (NMs) from agricultural wastes (AWs) and their possible applications in various industries to reduce the accumulation of AWs. By analyzing different synthesis methods (carbonized or uncarbonized), synthesis conditions, and sources of AWs, the study revealed the main approach for the synthesis of NMs from AWs. In general, the main types of NMs synthesized from AWs could be classified as carbon nanofibers (CNFs), graphene oxide (GO) and carbon nanotubes (CNTs), activated carbons (ACs) or biochars (BCs), nanocellulose, and carbon quantum dots (CQDs). There are many types of applications for these materials, some of which are available in the energy, medical, and environmental fields. Here it is necessary to highlight the application of these NMs in agricultural wastewater treatment. These NMs could be used as good adsorbents to treat various forms of wastewater from agricultural production activities. This wastewater might contain pollutants from multiple sources (i.e., heavy metals, pesticides, organic pesticides, fuels, and eutrophic waters), and NMs are capable of optimally removing different pollutants. Overall, the synthesis of NMs from AWs is a green and sustainable approach. It not only reduces the accumulation of AWs and avoids the waste of biomass but also reduces the synthesis cost of NMs and eliminates harmful chemicals from the environment, thus promoting the green synthesis of NMs.

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Keywords

Agricultural waste · Biomass · Nanomaterials · Pyrolysis · Remediation

15.1 Synthesis of Nanomaterials from Agro-wastes

As agriculture becomes more automated, the amount of agricultural wastes (AWs), the world's most widely sourced waste (i.e., straw produced during agricultural production, including rice straw, hulls, stalks, and corn cobs), is increasing every year. The large amount of AWs not effectively used and disposed of leads to a serious waste of resources. How to use and transform these materials in a rational manner has become an environmental issue of great concern. However, a large amount of AWs is not effectively utilized and treated, which leads to a serious waste of resources (Awogbemi and Von Kallon 2022). Therefore, this is an urgent issue to be solved, and the rational use and conversion of these substances have become a global and highly concerned environmental issue. This implies that if AWs are not treated effectively, serious environmental pollution problems will arise, thus affecting the natural environment on which human beings depend.

Recycling AWs without secondary pollution is not easy to achieve, as burning wheat straw and rice straw could weaken the original resources of the soil and thus lead to a decrease in soil productivity (Saharan et al. 2021). It is impossible to achieve the complete utilization of AWs without any side effects. Therefore, a large amount of research would be focused on how to reduce the generation of AWs while increasing the recyclability of AWs. That implies the conversion of generated AWs into other useful substances or materials for resource sustainability.

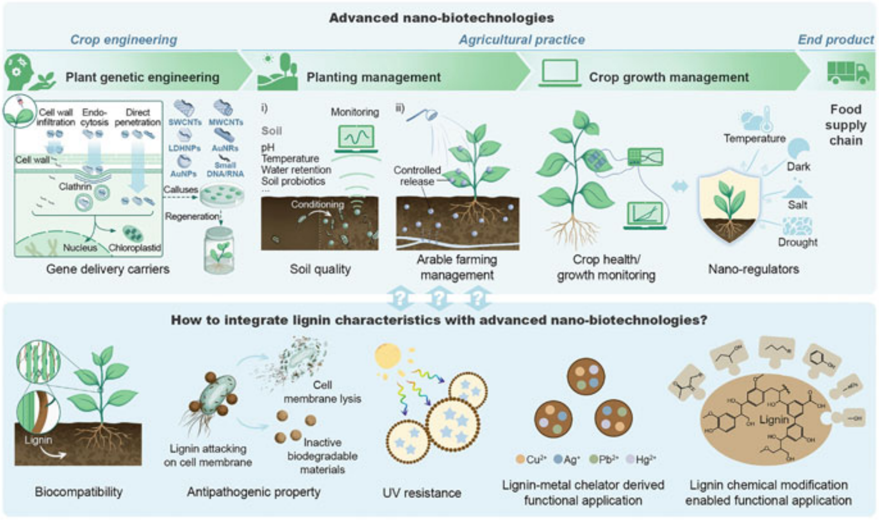
AWs are generally considered to have a high content of elemental carbon and nitrogen. Some AWs may also contain inorganic minerals (i.e., SiO_2 and Fe_3O_4) (Nehra and Chauhan 2022). Therefore, AWs could often be made into a variety of effective and environment-friendly materials. The composition of AWs is determined by the type of agricultural production activity (i.e., self-sufficient agriculture, intensive agriculture, extensive agriculture, commodity agriculture) and the form of agriculture (i.e., ecological agriculture, three-dimensional (3D) agriculture, organic agriculture, intensive agriculture, irrigation agriculture, etc.). Soil type and various natural environmental factors (i.e., local altitude and climatic conditions) could also alter the AWs to contain soluble components (i.e., organic acids) and insoluble components (i.e., lignin and cellulose). Depending on the composition and structure of AWs, AWs could be prepared or converted into many types of substances and functional materials.

In recent years, nanomaterials (NMs) have rapidly occupied the market of major industries as a new type of diversified materials. Among them, manufacturing industry, electronic products, and environmental protection industry have responded very strongly to NMs. Nanoelectronic components, nano-pharmaceutical products, and nano-adsorbents have been applied globally and in a large scale. Fortunately, AWs are promising raw materials for NMs. Studies have revealed the efficiency and economy of AWs, which can be cost-effectively converted into different nanostructured materials such as nanowires, nanosensors, nanotubes, and nanofibers. These materials have attracted great interest in many fields due to their unique properties. In this review, the integration of multiple NMs prepared with AWs (i.e., carbon nanofibers (CNFs), graphene oxide (GO) and carbon nanotubes (CNTs), activated carbons (ACs)/biochars (BCs), nanocellulose, and carbon quantum dots (CQDs) was concentrated. A comprehensive review was conducted using different preparation methods, preparation conditions, and types of AWs.

15.1.1 Conversion Process of Agricultural Waste to Carbonized Materials

15.1.1.1 CNs

CNFs are advanced in removing pollutants as an emerging and efficient adsorbent. Unlike the mode of action of CNTs and GO, this could also be an emerging and efficient alternative use for AWs. Unlike carbon fibers, CNFs are specifically applied to manufacture high-performance fiber-reinforced composites for aeronautic and astronautic as well as automobile industries. CNFs are more commonly used in composites, supercapacitors (SCs), catalyst support, solar cells, sensors, and thermoacoustics, as shown in Fig. 15.1 (Fu et al. 2022). Several methods could be used in the production of CNFs, such as chemical vapor deposition (CVD), laser ablation, and arc discharge (Mamun et al. 2016). Among them, CVD is generally considered to be the most reliable method, which synthesizes CNFs on different



Trends in Biotechnology

Fig. 15.1 Summary of carbon nanofiber applications (Fu et al. 2022) substrates. The simplicity and reliability of CVD have aroused great interest (Mamun et al. 2016). The advantage of using CVD to synthesize CNFs is that the crystallinity, internal molecular orientation, and diameter can be achieved through strictly controlled and precise synthesis conditions. A study has provided a relatively complete synthesis method (Ingale et al. 2021). The AWs were washed, dried, and then cut into small pieces. These small pieces were subjected to a pyrolysis process in a CVD apparatus at a temperature of 800–850 °C (with argon as the carrier gas). Pyrolysis was carried out for 1–2 hours, and then the furnace was cooled to room temperature, during which time the CNFs were deposited in quartz bowls, cooled, cleaned, and collected. An effective carbon fiber composition was obtained and generally used in environmental industry as well as light industry due to its high elemental C content and unique structure.

CNFs with large specific surface area, high electron transfer rate, and outstanding chemical stability have received extensive attention as SC electrodes. In terms of thermal stability, carbonization, and electrospinning, AWs have been stagnant in the preparation of CNFs. With the continuous progress of scientific research, recyclable molten salt, which is a new method, has been discovered and successfully applied to the preparation of carbon NMs (Kamali and Fray 2013). In this method, NaCl and a small amount of NaOH are mixed as the molten salt. First of all, NaOH not only reduces the total melting point of molten salt but also constructs a liquid medium for carbonization. This medium is a relatively moderate carbonization condition for fibers to ensure that CNFs maintain the fiber structure during carbonization. The molten salt then acts as an intercalator, and a barrier is created between the fibers, which effectively prevents sticking and clumping between fibers. Finally, the increase in the specific surface area of CNFs is facilitated by the gentle activation with few NaOH. According to this approach, CNFs are prepared by direct carbonation at 900 °C. Then, centrifugal washing is used for the isolation of CNFs. And the mixed salts could be recovered from the supernatant and reused later.

15.1.1.2 GO and CNTs

Typically, AWs contain many hydrocarbon precursors, which are currently an important source of hydrocarbons as they are renewable, economical, and susceptible to the synthesis of different carbon nanostructures (Shah and Aziz 2020). Different types of AW have the potential to synthesize different carbon nanostructures, for instance, to produce graphene and CNTs on an industrial scale (Shah and Aziz 2020). This is very promising and is currently one of the most significant nanotechnologies. Overall, the use of AWs is considered to be sustainable. AWs could be produced in scalable quantities, which are environment-friendly and cost-effective. Through various means, AWs are transformed into high-quality CNTs and graphene structures that are beneficial for advanced electronic and energy applications in different fields.

Studies have validated the potential of AWs for the synthesis of GO; however a complete review on the differences between different AWs as well as different methods for GO synthesis composition is missing. GO is widely used in many fields, such as optoelectronics, biomedical signal receptors, and electronic sensing elements (Awogbemi and Von Kallon 2022). And the preparation of GO by AWs is a promising method. Some studies have shown that sugarcane bagasse is a good material for synthesizing GO. Sugarcane bagasse contains a large amount of cellulose, hemicellulose, and lignin and a small amount of unusable ash (1–4%). These carbonaceous by-products are particularly important in the synthesis of GO. In addition, significant amounts of soluble/insoluble carbohydrates, essential oils, cellulose, and hemicellulose were observed in orange peel. Also in the rice bran from agricultural production, significant amounts of protein, fat, and minerals and small amounts of ash were found. All of these AWs are carbonaceous products but are essential to the GO production process. Most of the AWs preparation of GO followed an earlier approach by pyrolysis of the available fiber fraction from AWs. GO was produced by oxygen-limited high temperature in a muffle furnace. Current studies have focused on the effects of different sources of AWs, different pyrolysis temperatures, and different pyrolysis times on GO production. This technology is considered as a potential economic recycling technology and is becoming one of the most promising means in the Anthropocene.

Research on CNTs has been conducted for more than 25 years. Due to their excellent properties (i.e., large surface area, high elastic module, high conductivity, strong tensile strength), they are ideally applied in many fields. Previous studies have shown that many organic/inorganic contaminants in the environment could be removed by CNTs as an efficient NM (Wu et al. 2016). It is particularly important to synthesize CNTs via economical and recyclable methods. Current research indicated that AWs could be an effective material for CNT production. Natural AW products are inexpensive and should be used as precursors for hydrocarbons. In some recent studies, using BCs as precursors, CNTs have been synthesized by microwave irradiation (Kumar et al. 2016). BC is a complex carbon material produced by pyrolysis of biomass. At present, eco-friendly precursors and better methods are still being studied to produce cheaper CNTs on a larger scale. In addition, new manufacturing technologies for CNTs might be the result of large-scale and more economical production. Apparently, the sources of these AWs are readily available and inexpensive, and due to their volatility and nontoxicity, there is no need to worry about their cumulative toxicity in the chemical environment. Currently, the process of producing CNTs from AWs for the manufacturing of raw materials for optical and electronic sensing elements has been quite mature. The preparation of CNTs is becoming a completely new way to recycle AWs.

15.1.1.3 Activated Carbon/Biochar

BC/AC has been used in a wide range of applications as an effective material for removing various heavy metal contaminations and organic pollutants, an efficient pollutant scavenger, and a catalyst for efficient chemical reactions. BCs/ACs produced from AWs are nonselective for many metals. BCs produced from various AWs, such as plant waste, vegetable/fruit waste husks, tea waste, shell of nuts, sawdust, straw, and rice husks, have been used to remove various harmful heavy metals from contaminated water (Nguyen et al. 2022). Currently, BCs produced from AWs are used to improve their adsorption efficiency and increase their access,

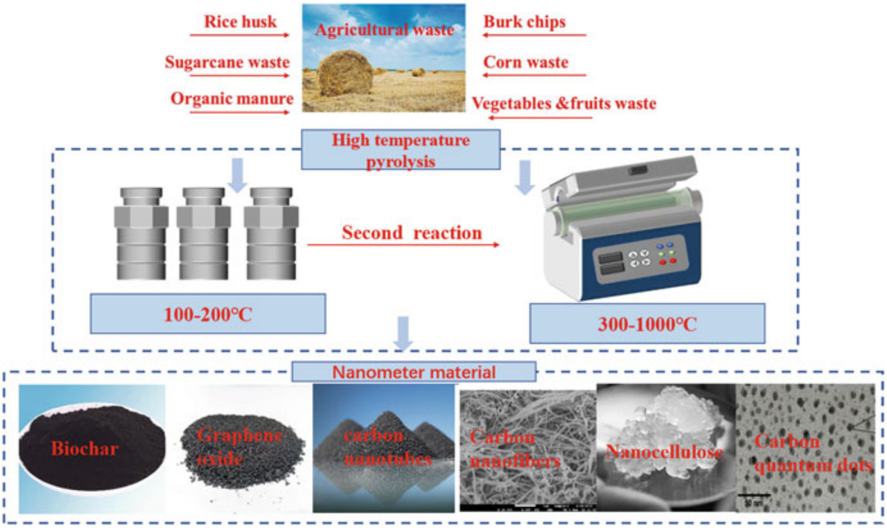


Fig. 15.2 Conversion of agricultural waste to nanomaterial (Nguyen et al. 2022; Saharan et al. 2021; Shah and Aziz 2020; Mamun et al. 2016; Lin et al. 2014)

such as controlling the pyrolysis temperature, and adjusting the pyrolysis environment (nitrogen conditions, flow rate) and auxiliary pyrolysis substances (metallic and nonmetallic, organics). These could have a significant impact on the conditioning of BCs, and some methods such as ball milling and secondary pyrolysis can also refine BCs in terms of its properties as NM.

In addition to high-temperature pyrolysis, the hydrothermal method has become an effective method for synthesizing BCs, which could effectively load various functional groups and available substances onto the nano-BCs (Fig. 15.2). Deionized water (20 mL) was used to dissolve 0.25 of g $Cu(NO_3)_2–3H_2O$, and Cu (II) solution was added dropwise into a three-necked flask containing deionized water through a funnel. The mixture was stirred continuously at 40 °C for 5 h. Then $NH_3–H_2O$ was added to adjust the pH of the mixture to 8. The mixture was transferred to an autoclave of stainless steel D and heated at 170 °C for 7 h. The resulting precipitate was then filtered and washed three times with deionized water and ethanol successively. Finally, the precipitate was vacuum-dried at 80 °C for 24 h. The evaporated water produces an effective BC component, which is more complex than the conventional pyrolysis method but relatively effective for improving the performance of nano-BCs.

15.1.2 Conversion Process of Agricultural Waste to Non-carbonized Materials

15.1.2.1 Nanocellulose

Generally, cellulose is a material that is important in maintaining the cell wall structure of plants and is strong, insoluble in water, and fibrous. It has potential for use as a reinforcing material because it is cost-effective, lightweight, sustainable, biodegradable, and soft compared with hardwoods. The main part of cellulose in forests is lignocellulosic fibers, with wood being the most important source. Other products that contain cellulose include AWs, aquatic plants, algae, grasses, and other plant matters (Khan et al. 2018). They contain not only cellulose but also hemicellulose, extractives in relatively limited amounts, and lignin. The production of commercial cellulose is mainly concentrated in harvest sources such as AWs. For example, cotton is a high-purity AW (Khan et al. 2018).

The application of nanocellulose in different fields such as material science and biomedical engineering has gradually attracted attention. In general, Nanocellulose has some outstanding features such as abundant functional groups, unique optical properties, excellent mechanical properties, good biocompatibility, low cytotoxicity, and large specific surface area. Cellulose is the most abundant among the plant skeleton components, and usually AWs contain large amounts of cellulose that can be used to produce nanocellulose. Nanocellulose can be prepared by enzymatic, physical, or chemical treatment of AWs. The hemicellulose and lignin in AWs are first removed, and then the lamellar structure of the cellulose is deconstructed (Khan et al. 2018). The nanocellulose prepared by AWs is usually categorized into two types: cellulose nanofibers and cellulose nanocrystals. Cellulose nanocrystals, which are 20–100-nm long, can be obtained by acid hydrolysis. Cellulose nanofibers are individual nanoparticles with lengths of a few micrometers and transverse dimensions of approximately 5 nm. The size of both nanocelluloses depends on the preparation process and raw materials (Fei et al. 2019).

Nanocelluloses in the aqueous dispersions could easily form 3D networks through hydrogen bonding and physical connections. In addition, their abundant functional groups and great hydrophilicity are beneficial to the production of hydrogels. When the concentration of cellulose nanocrystal aqueous suspension achieves the critical value or when salt or acid is added, it becomes a gel. As the concentration of cellulose nanofibers increases, the rheological behavior of cellulose nanofiber systems changes from low-viscosity suspensions to high-viscosity gels. It occurs even at a low concentration of 0.125 wt%. However, the hydrogels formed by various nanocelluloses are independent of their origin. The surface morphology of cellulose nanocrystals and cellulose nanofiber hydrogels is different. To be specific, cellulose nanofibers exhibit fibrous networks with different thicknesses, but cellulose nanocrystals exhibit a leaf-like network structure. Cellulose nanocrystal/cellulose nanofiber composite hydrogels have more interconnections and richer pore structures than their individual cellulose nanofiber or cellulose nanocrystal counterparts. It was shown that the mechanical strength of hydrogels was significantly affected by the aspect ratio of nanocelluloses (Al-Sabah et al. 2019). The tensile properties of the composite hydrogels are enhanced by cellulose nanofibers and cellulose nanocrystals. A well-defined matrix with excellent biocompatibility with human cells is provided by the plant-derived nanocellulose hydrogels. This matrix simplifies the recovery of cells from the scaffold to be used in further. The safety and effectiveness of the nanocellulose hydrogel drug delivery systems have been tested and assessed through choroid, blood compatibility, apoptosis, and animal in vivo. Therefore, nanocellulose-based hydrogels have been proven to be promising and safe drug carriers.

Cellulose nanocrystals could be efficiently produced using physical, chemical, and combined physical–chemical methods. The researchers used acid hydrolysis to prepare cellulose nanocrystals from corn husks and showed that the process of treatment and bleaching through alkali resulted in the most pronounced crystallinity index of cellulose nanocrystals (68.33%) and showed the most significant and sharpest peak at $2\theta = 22$. The increased crystallinity of treated corn hulls compared with untreated hulls may be due to the different levels of complexity and rarity of the unidentified non-cellulosic materials. Furthermore, as a part of this analysis, chemical treatments could be used to improve the component of cellulose and nanocellulose. As a representative physical processing method, electrospinning is a technology that applies external force to the polymer solution and is popular in the processing of micro-fibrillated cellulose. Because the surface tension of the polymer is separated by electrostatic repulsion in the liquid system, the jet of polymer solution is discharged at a very high strain rate through high-pressure microfluidizers into micro cellulose collectors that mainly rely on nanocellulose fibers from various sources (banana tree, grasses, and flax). In addition, steam explosion and ultrasound are effective physical methods for preparing nanofibers. Sophisticated techniques tend to be most effective in retaining the active components of cellulose. Cellulose was extracted from sugarcane bagasse through xylanase pretreatment and bleaching processes as well as steam explosion. Chemical analysis showed that the extracted cellulose was higher and the hemicellulose and lignin content was lower compared with the crude material. Furthermore, pretreatment with xylanase could effectively reduce the discoloration caused by 23% of the compounds. Currently, the reuse industry of AW has been reflected in several NM fields, and the extraction technology of nanocellulose will certainly become a hot issue for future research due to its outstanding properties. Because the physical, chemical, mechanical, and even biological characteristics of the material are influenced by the nanocellulose, the properties of the enhanced nanocellulose affect the performance of the target material. Nanocellulose could also be extracted from the industrial waste of sawn wood. A new approach for improving the quality of nanocellulose is the microbial pretreatment of waste with white-rot fungi (*Echinodontium taxodii*) to eliminate lignin and improve nanocellulose separation (Mautner 2020).

15.1.2.2 Carbon Quantum Dots

CQDs are composed of sp2/sp3 hybridized carbon atoms. In 2004, CQDs were discovered during the purification of single-walled CNTs (Huang et al. 2017). They have good dispersibility and solubility in aqueous and organic solvents, polychromatic emission, and dependent/independent excited fluorescence, among other properties that deserve further investigation.

A previous study proposed a method for efficient extraction of CQDs from waste bagasse (Kasinathan et al. 2022). A typically experimental procedure is documented as follows: First, 2 g of bagasse was mixed with 50-mL deionized water and stirred to homogenize the solution. Afterwards, ammonia was added dropwise into the precursor solution. The homogeneous solution was then transferred to the high-pressure autoclave of stainless steel and heated continuously for 12 h at 200 °C. After that, the reactive mixture was cooled to room temperature, and then a black precipitate formed. The mixed solution was ultrasonically treated for 1 h, followed by centrifugation at 5000 rpm for half an hour to remove undissolved particles. The supernatant was then filtered using a microporous membrane with a pore size of 0.22 μm for large-particle removal. Eventually, CQDs prepared from sugarcane bagasse were obtained for subsequent characterization and application. Due to their efficient photochemical reaction performance, CQDs are often used in a variety of applications of photocatalytic reactions, and through coupling with other substances, CQDs could efficiently realize the chemotherapy process of cancer (specific recognition and cleavage). In the application of environmental functions, CNTs are often used as efficient free radical catalysts to efficiently degrade a variety of pollutants (including heavy metals and refractory organic pollutants) in water. At the same time, due to the particularity of its structure, CQDs can also be quickly combined with a variety of environmental materials and more efficiently adsorb and remove refractory pollutants in the environment through joint action (Ahuja et al. 2022).

15.2 Characterization of Nanomaterials From Agricultural Waste

The physical–chemical properties of NMs generally include their size, shape, surface area, surface, and structural properties. These properties are generally determined by the AWs and production conditions (i.e., generation method, time, and temperature). In the early stages of experiments, researchers often determine whether these properties need to be characterized based on the purpose of the study. The results of characterizing and quantifying the surface and structural properties of NMs are important for their practical applications in agriculture or the environment. Figure 15.3 summarizes some of the properties that are often characterized in most studies of NM.

The same as other ordinary NMs, the size and distribution of NMs from AWs affect the degree of reaction with other compounds, and small-sized particles react more strongly than large-sized ones. Meanwhile, the surface area of NMs is an important property that plays a role in their adsorption, catalysis, and electrochemical sensing applications. NMs with larger surface area can be readily adjusted to improve mechanical properties such as hardness, adhesion, and stress. Currently, NMs with specific shape and desired particle size could be prepared by controlling

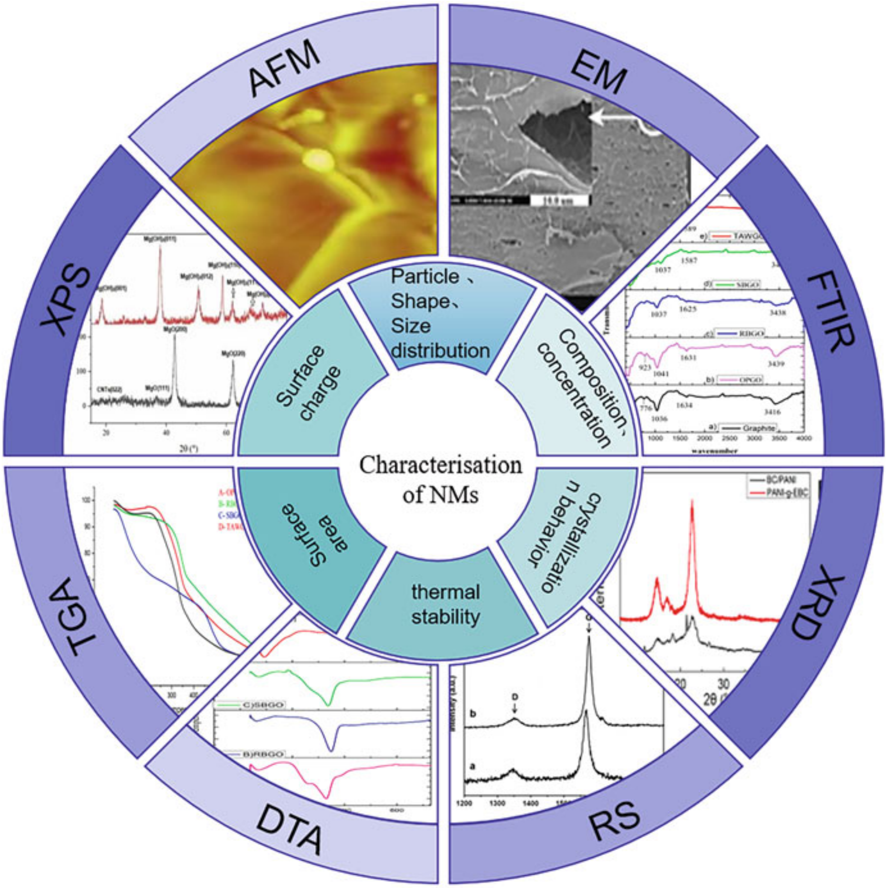


Fig. 15.3 Summary of different characterization methods for nanomaterials (McCarron and Chambers 2021; Merugu and Gothalwal 2021; Seifi et al. 2020; Fei et al. 2019; Ingale et al. 2021; Zhong et al. 2022)

the synthesis process and reaction conditions, and these NMs have better experimental effects in different fields of practical applications.

However, unlike ordinary NMs, some NMs from AWs have organic structures that construct rich porous structures and increase the specific surface area. The adsorption of contaminants by these NMs is also dependent on functional groups of carbon materials, such as carboxyl or hydroxyl groups, and the immobilization of heavy metals is achieved by surface precipitation, electrostatic attraction, and complexation with them. The adsorption of NMs is increased by the electrostatic gravitational force of carbon. The adsorption of positive ions, such as heavy metals and ammonia, could be enhanced when the NM surface is negatively charged, while the adsorption of negatively charged ions (e.g., phosphates) can be achieved when the surface of NMs is modified to be positively charged. The mineral composition increases the adsorption capacity of NMs, such as CO_3^{2-} and PO_3^{2-}, which favors the adsorption of metals, such as Pb.

In addition, many factors, including composition, temperature, and bonding interactions between functional groups, may affect the structure of NMs. A comprehensive understanding of the crystallization behavior is required to predict the structure–property correlation of NMs. The results of several studies have shown that the crystal structure and crystallization behavior of nanocomposites and pure NMs are not the same for both. At the same time, the elemental composition and mass concentration of NMs are two factors that must be considered prior to practical application. A necessary feature to assess the composition and purity of NMs is to characterize the chemical composition of NMs, especially during synthesis and formation.

The performance and application of NMs are mainly determined by their chemical composition, surface morphology, and other factors. The study of these factors helps classify different NMs and makes them more appropriate for practical applications. Several techniques for the characterization of NMs are briefly described below, along with their applications, advantages, and limitations.

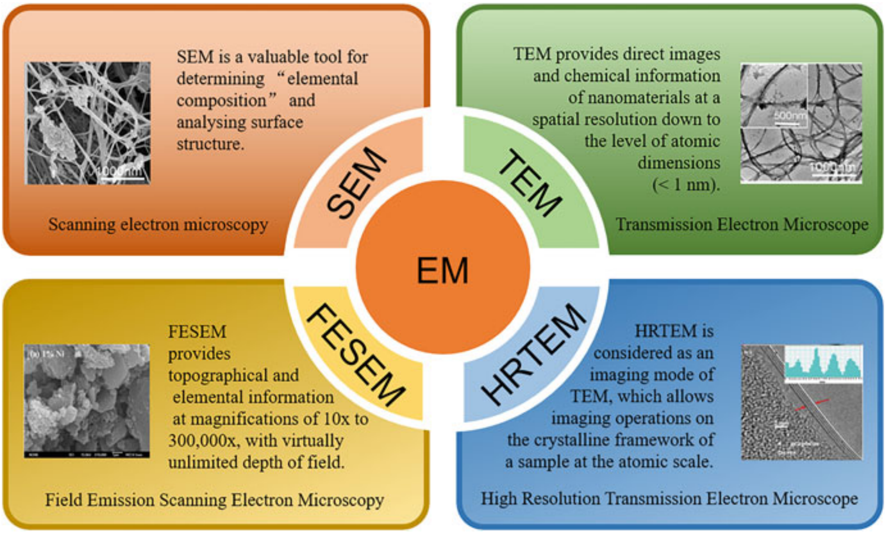
15.2.1 Technique of Microscope

15.2.1.1 Electron Microscope

Electron microscopy (EM) is used as the preferred technique to determine the surface characteristics, shape, and size (distribution) of NMs. It not only measures the resolution of individual particles but also distinguishes and determines the primary particles in aggregates and epimers. Figure 15.4 summarizes the characterization of NMs by different EMs, listing their advantages and disadvantages. At the same time, EM is suitable for the determination of a large number of samples. Because it can be coupled with different measurement systems, it facilitates a wider range of analytical measurements (McCarron and Chambers 2021). The two main types of EM are scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

SEM

SEM could be applied to observe the surface topography of the sample through the interaction between the sample with the electron beam. When the SEM is equipped with an energy-dispersive X-ray spectrometer (EDX) or a wavelength-dispersive X-ray spectrometer (WDX), it can be used as an electron probe to simultaneously perform the functions of detecting X-rays, reflected electrons, oscillating electrons, cathode rays, and transmitted electrons emitted from the sample. The shape and size (distribution) of NMs could be directly obtained from the results of scanning samples by SEM. But most EC techniques would damage the prepared samples, excluding SEM. In addition, due to fewer sample particles in the scanning region of



SEM is a valuable tool for determining "elemental composition" and analysing surface structure.

Scanning electron microscopy

TEM provides direct images and chemical information of nanomaterials at a spatial resolution down to the level of atomic dimensions (< 1 nm).

Transmission Electron Microscope

FESEM provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field.

Field Emission Scanning Electron Microscopy

HRTEM is considered as an imaging mode of TEM, which allows imaging operations on the crystalline framework of a sample at the atomic scale.

High Resolution Transmission Electron Microscope

Fig. 15.4 Summary of multiple electron microscopy techniques for the characterization of nanomaterials (Kumar et al. 2016; Merugu and Gothalwal 2021; McCarron and Chambers 2021; Lin et al. 2014)

the SEM, there are deviations in the detection of the size distribution of heterogeneous samples (Ingale et al. 2021).

TEM

In addition to determining the surface morphology, shape, and dimensions of the NM, TEM could also determine the crystal structure of materials and their sample defects. TEM has a higher resolution than SEM, and the resolution of this technology could be as low as 1 nm. However, the sample preparation process prior to the use of TEM is very complex and time-consuming. Because the measurements of TEM require that the thickness of the sample to be analyzed is very thin (50–150 nm) or almost transparent, this facilitates the passage of electrons through the sample to produce high-resolution images.

In general, the degree of aggregation as well as dispersion, shape, and size of NMs could be determined by TEM and SEM. However, compared with SEM, TEM has richer measuring function and higher spatial resolution.

Other Electron Microscopy Techniques

A transmission electron microscope operating in the scanning mode is called STEM, TSEM, or T-SEM. When combined with a high-angle annular dark-field (HAADF) detector, scattered electron images with different contrasts are displayed by HAADF-STEM to reveal the crystallinity and chemical composition of the samples. The convenience of this technique compared with other analytical techniques is that there is no sample staining process before analyzing biological samples. Due to its high-resolution properties, high-resolution transmission electron microscopy (HRTEM) has become a common tool for studying and analyzing crystalline materials with nanoscale properties (Zhong et al. 2022). Compared with conventional microscopy techniques, HRTEM could neglect the amplitude of the sample during the absorption process in the image development phase (Kumar et al. 2016).

15.2.1.2 Atomic Force Microscopy (AFM)

Scanning probe microscopes (SPMs) are used to measure the physical properties and surface topography of samples. The main types of SPM are AFM, NSOM (Near field scanning optical microscopy), and STM (Scanning tunneling microscope); about 80% of the SPMs on the market are AFMs (Merugu and Gothalwal 2021).

AFM, an imaging technique, could be used to determine the agglomeration, aggregation, surface properties, shape, and size distribution of NMs as well as to detect and measure the size of particles in aggregates and attachments. Comparison of AFM with DLS (Dynamic light scattering) and EM (Electron microscopy) showed that AFM provides better particle-size characterization results than other techniques (Lin et al. 2014). AFM also requires little sample preparation and can also be used to analyze a variety of different sample types, including biological, carbon-based, core/shell, inorganic, and organic materials and mixtures of different covers and shapes (Lin et al. 2014).

15.2.2 Techniques of Spectroscopy

15.2.2.1 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR can be used to determine the functional groups (i.e., aliphatic or aromatic properties) of NMs. The performance of FTIR is excellent. The specific performances are high sensitivity, fast analysis, no damage to samples, less sample consumption, convenient operation, and wide application range (suitable for solid, liquid, or gas samples; it can also detect inorganic, organic, and polymer compounds). Attenuated total reflection (ATR–FTIR) spectroscopy could detect the molecular structure of adsorbed/deposited species at the solid/liquid or solid/air interface. Moreover, the complexity of sample preparation and the lack of spectral repeatability in the traditional transmission infrared mode are minimized or directly eliminated. The chemical composition and surface functional groups of the sample was determined by Infrared absorption spectrum using ATR–FTIR (Seifi et al. 2020). Although ATR–FTIR has been used to determine the surface characteristics of NMs, this surface analysis method is no longer sensitive at penetration depths beyond 500 nm.

15.2.2.2 Raman Scattering (RS)

RS could be used not only to identify chemical composition but also to provide information related to physical and structural characteristics. This technique is nondestructive and requires very few samples and has the advantages of being fast, convenient, and easy to use. However, Raman spectroscopy is difficult to interpret professionally. Compared with the traditional RS, surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS) could provide structural, chemical, and electronic properties, as well as the topological structure of NMs. But SERS measurements lack reproducibility due to the size and shape variations and poor aggregation of NMs.

15.2.3 Techniques for Thermal Analysis

The thermal analysis technique is a very important analytical test method to study various transformations and reactions of materials such as dehydration, crystallization-melting, evaporation, phase change, etc. as well as thermal decomposition processes and reaction kinetics of various inorganic and organic materials under programmed temperature control. Several thermal techniques are also available to assess the thermal stability and count the amount of NM coupling compounds. The thermal stability and thermal degradation behavior of NMs can be evaluated by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

15.2.3.1 DTA

DTA not only is an important method of thermal analysis but also completes the temperature difference test between a substance and a standard substance under programmed temperature control as a function of time or temperature. The peak value, area, number, position, and symmetry properties of the characteristic peaks on the difference heat map are clearly observed. The position, size, direction, and number of peaks of the sample indicate the conversion temperature of the sample changes, degree of thermal effect, positivity and negativity of the thermal effect, and number of sample changes, respectively. Under the same determination conditions, the characteristics of thermal spectra of many samples are obvious. Thus, sample-type confirmation can be achieved by comparison with the known thermal spectra. In theory, quantitation of substances could be achieved by peak area measurement. However, since DTA is affected by many factors, it is difficult to quantify accurately.

15.2.3.2 DSC

DSC is used to determine the power difference under programmed temperature control between the input material and the reference material as a function of temperature. The glass transition, crystallization, melting, and decomposition of NM biological couples could be determined by DSC. Thus, the stability and structure of the studied samples are obtained (Seifi et al. 2020).

15.2.3.3 Thermogravimetric Analysis (TG)

TG is a thermal analysis technique that is used to measure the mass of materials to be measured as a function of temperature at the program-controlled temperature in order to obtain the thermal stability and composition of the samples. TG could be used to monitor temperature-dependent weight changes in a large number of samples (e.g., various NM biocouples) (McCarron and Chambers 2021). In the measurement and analysis of samples, TG is combined with other analysis methods to conduct comprehensive thermal analysis and to comprehensively analyze materials.

15.2.4 Other Technologies

15.2.4.1 X-ray Diffraction

By analyzing the diffraction pattern of NMs by X-ray diffraction (XRD), the composition, structure, and morphology of atoms or molecules in the material can be obtained. XRD could be used for compositional analysis to determine the crystalline carbon of NMs. In addition, XRD spectroscopy can provide detailed information on some organic compounds such as lignin, cellulose, and hemicellulose. It does not contaminate and destroy the samples, and the measurement is rapid and highly accurate. Furthermore, a large amount of crystal integrity information could be obtained by it. However, there is a defect that the compound cannot be quantitatively analyzed (Kamali and Fray 2013).

15.2.4.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is currently widely used for surface analysis in research, with an information depth of about 3–5 nm. The valence of elements is determined by XPS based on the analysis of photoelectron energy distribution; in addition, it can be used to determine the relative abundance of different species of elements on the surface of a NM. However, data acquisition in XPS is performed at a specific point of the sample, but NMs are a nonhomogeneous mixture; the results of the analysis are strongly influenced by these measurement points (McCarron and Chambers 2021).

15.2.4.3 Electrophoretic Light Scattering (ELS)

The determination of zeta potential is often performed using ELS techniques, which allow simultaneous measurement of the velocity of a large number of charged particles in a liquid. However, ELS is still affected by electro-osmosis effects that reduce the accuracy and reproducibility of the measurement. At the same time, zeta potential is sensitive to changes in environmental factors, including pH and ionic strength. Therefore, the zeta potential measured in dilute solution is not accurate.

15.2.4.4 Brunel–Emmett–Taylor

Brunel–Emmett–Taylor (BET), a common method for calculating the surface area of NMs, could be used not only to analyze the specific surface area of solid samples by gas adsorption but also to determine the porosity and pore-size distribution of samples through gas absorption and mercury intrusion porosometry (McCarron and Chambers 2021). However, this method requires theoretical values and computational analysis, so the measurement results may vary due to different analysis conditions (i.e., gas and pressure). To remove other volatile contaminants or water, samples must be degassed prior to measurement. Therefore, the BET could be time-consuming due to extensive sample preparation before analysis.

15.3 Potential Applications of Agro-waste-Based Nanoparticles

15.3.1 Applications of Agro-waste-Based Nanoparticles in Energy

With the rapid development of the global economy and the extensive use of fossil fuels, resource shortages and environmental pollution have become increasingly prominent. Therefore, some renewable energy sources, such as tidal, solar, and wind power, have been developed. However, this sort of energy industry is limited by the intermittent and regional of applications. To ensure the normal transmission of energy, energy storage devices need to be developed. Due to the structural stability, large specific surface area and porosity, high electrical conductivity, and low density, many carbon NMs such as CNTs, OLCs (onion-like carbons), AC (active carbon), CDC (carbide-derived carbon), CA (carbon aerogel), and graphene (Fig. 15.5) have promising applications in the storage and conversion of energy.

15.3.1.1 Energy Storage

CNM-Based Lithium (Li)–Ion Battery

Electrochemical energy storage and conversion, such as fuel cells, Li sulfur batteries, Li–ion batteries, metal–air batteries, and SCs, could realize chemical and electrical energies through reversible redox reactions with maximum conversion efficiency of energies to improve the efficiency of energy utilization. Rechargeable Li–ion batteries and ideal energy storage containers have been widely applied to some portable electronic devices, such as mobile phones and laptops. The advantages are green environmental protection, long cycle life, and high energy density. Graphite,

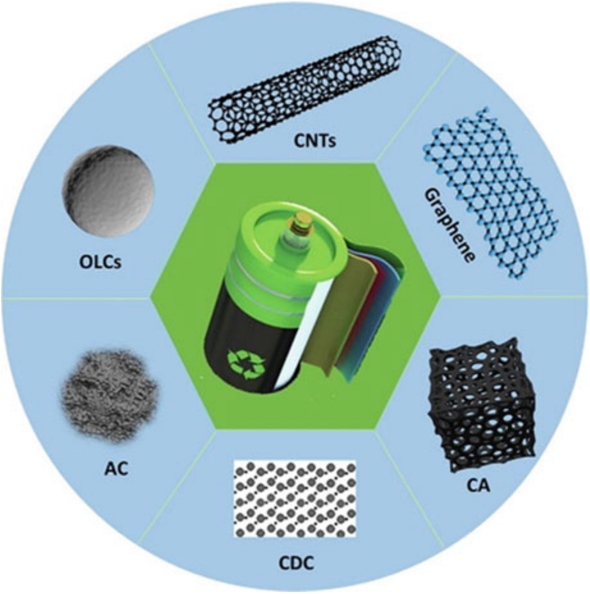


Fig. 15.5 Several mainstream carbon materials have been applied in batteries (Zhai et al. 2022)

the main anode material for Li–ion batteries, has some defects due to its low theoretical specific electricity (372 mA h g^{-1}), which resulted in Li–ion batteries not being used for the energy storage of grid-level and electric vehicles. During the initial charge–discharge process, solid–electrolyte interfacial film consumes a large amount of Li ions in the cathode material, resulting in an initial columbic efficiency below 70%, which inevitably leads to a large reduction in specific capacity and energy density. In response to this problem, some researchers developed a pre-lithiation strategy to embed Li metal particles on the surface of porous carbon nanotubes (PCNTs), which is used as anode material for batteries of Li ion. The results showed that the initial columbic efficiency was effectively increased to 96%. The reversible capacity was as high as 932 mAh g^{-1} at a current density of 20 mA g^{-1}. The rate performance and cycling performance were also very satisfactory. The reversible capacity reached 530 mA h g^{-1} after 230 cycles at a high current density of 200 mA g^{-1}, which was much higher than commercial graphite rate and produces almost no toxic and harmful pollutants. Carbon-based materials are widely applied for the preparation of electrode materials for Li–ion batteries, and functionalized carbon nanocomposites have significantly improved the electrochemical performance of anode materials. A mixture of graphite and 5–10% silicon has been reportedly used as anode material for industrial Li batteries to achieve an increase in the energy density of the battery. Pre-lithiation of carbon NMs could significantly improve the initial columbic efficiency of Li–ion batteries.

CNM-Based SCs

As a highly efficient electrochemical energy storage device and a bridge between capacitors and traditional batteries, SCs have broad application prospects. However, the relatively low energy density of these SCs still hinders their large-scale practical applications. The properties of the electrode materials largely determine the SC charge storage capacity. Study prepared a 3D graphene/carbon nanotube (3DG/CNT) as electrodes for electric double-layer capacitors by CVD. The structure of this material is layered, in which the CNTs are effectively embedded in the graphene to foam layer. The synergistic effect of CNTs and graphene could be exerted. On the one hand, the support platform required for CNTs could be provided by graphene foams; on the other hand, CNTs can reduce the influence of graphene layer defects on the electron transport rate and electrical conductivity. This composite material has high specific capacitance, excellent rate performance, and good stability (Chang et al. 2022). For example, several researchers have developed an N–doped CNF with hollow particles by electrospinning and carbonization. During the period of synthesis, electrospinning could form one-dimensional (1D) composite precursors. As an electrode, the nanofibers have a layered porous structure with high N-doping contents, and the assembled SC devices exhibit superior SC performance and good cycle stability (only 1.8% loss of capacitance over 10,000 cycles) under various current densities. The research encapsulated NiO into mesoporous carbon spheres to prepare composites (NiO/mesoporous carbon nanospheres, NiO/MCNs). NiO particles embedded in carbon not only provide pseudo capacitance but also promote partial graphitization due to the fast and reversible faradaic redox reaction, which optimizes the crystal structure of carbon matrices, leading to greatly improved electrochemical performance. The specific capacitance in a 6-mol L^{-1} KOH electrolyte solution reaches 406 F g^{-1} at the current density of 1.0 A g^{-1}. At 3.0 A g^{-1}, its electrochemical stability is excellent with a capacitance retention of about 91.0% after 10,000 cycles of cycling. The cycling stability and specific capacity of capacitors are largely determined by the electrode materials of SCs. Therefore, the development of highly active electrode materials plays an important role in optimizing the electrochemical performance of capacitors. Porous carbon materials act as a good carrier, and through chemical modification, FCMs possess stronger electrochemical activity. With the improvement of the preparation process and the reduction of the preparation cost, the FCM-based composites will receive more research and attention in the electrode development of SCs.

15.3.1.2 CNMs to Product Hydrogen

The environmental pollution and energy shortages caused by the overuse of fossil fuels have led to an urgent need for the development of sustainable energy sources. Hydrogen energy has the advantages of high combustion heat and nonpolluting products and is considered to be one of the most ideal energies in the future. Among many hydrogen production methods, the photocatalytic hydrogen production technology has become a popular research area for hydrogen production due to its green, sustainable, and widely distributed solar energy. Two-dimensional (2D) carbon NMs stand out among many photocatalytic hydrogen production materials due to their good stability, outstanding mechanical properties, excellent electrical conductivity, ultrahigh ion adsorption, and large specific surface area (Xiong et al. 2022). At present, domestic and foreign researchers have carried out a number of studies on the photocatalytic hydrogen production technology of 2D carbon NMs, which are mainly divided into the following categories:

Graphyne

Graphyne is an emerging 2D carbon material after the development of fullerene and graphene. It is the most stable diacetyl–lenic carbon allotrope that has ever been synthesized. Butadiyne (sp carbon atom), benzene ring (sp2 carbon atom), and π-connected structures are composed of well-dispersed electron-rich cavities. According to the number of acetylene bonds between the two aromatic rings, graphyne is divided into GY (one acetylene bond), GDY (two acetylene bonds), graphyne-3 (three acetylene bonds), and graphyne-4 (four acetylene bonds). GDY, an electronic semiconductor with direct band gap and tunable band structure, is the most stable carbon-based allotrope among diacetylene groups. The high structural shearability of GDY makes it easy to achieve general molecular design and element doping. The low-temperature requirement for GDY synthesis can perfectly maintain its unique structural advantages of diacetylene bonds, which will compensate for the traditional sp2 hybridization. Compared with other carbon materials such as graphene and CNTs, GDY is sufficient in synthesis and application. The high mechanical strength and flexible morphology of GDY have led to its widespread use in gas separation membranes, energy storage, photocatalysis, and battery anode materials, which feature controllable pores and additional electron-rich diacetylene bonds in the conjugate plane. For example, some researchers introduced g-C_3N_4 nanosheets into GDY using the π–π stacking method, which successfully prepared g-C_3N_4/GDY nanocomposites with 1% GDY content. In the infrared spectrum, the overlapping peaks of g-C_3N_4 and GDY represent the successful construction of the heterojunction. Due to the in situ construction of the g-C_3N_4/GDY heterojunction, not only the band gap width of g–C_3N_4 is optimized, but also the recombination of hole pairs and photogenerated electron is greatly alleviated. Finally, the hydrogen production rate increased to 454.3% μmol h^{-1} compared with that of g-C_3N_4.

Covalent Organic Frameworks (COFs)

2D COFs are a class of organic crystalline porous materials with large specific surface area, tunable pore size, conveniently functional modification, and highly ordered pore structure and can be synthesized using diverse methods. As an emerging class of heterogeneous catalysts, COFs have been widely used in the fields of gas storage and separation, drug delivery, catalysis, optoelectronic devices, SCs, and batteries. Under sunlight irradiation, the valence band electrons of COFs are excited to the conduction band. To achieve the separation of electron and hole pairs, the electrons in the highest occupied molecular orbital (HOMO energy level) are excited to the lowest unoccupied molecular orbital (LUMO energy level). According to the catalyst design method, COF catalysts can be divided into two categories of intrinsically supported types. Among them, the design method of intrinsic COFs catalysts is based on the "bottom-up" strategy, which embeds the catalytic active centers in the material nano-framework. Using supported COFs as a carrier, metal particles and ions were loaded onto the surface of COFs through subsequent modification methods. For example, researchers have reported the preparation of 2D sp2-carbon-conjugated COFs composed of ERDN, PDAN, and TFPPy (1,3,6,8-tetrakis (4-formylphenyl) pyrene) (denoted as sp2c-COFERDN), which confirmed the enhanced light absorption and improved charge transfer. Sp2c-COFERDN could exhibit good photocatalytic hydrogen production performance when Pt nanoparticles are used as co-catalysts.

Transition Metal Carbon/MXene

With the successful development of the layered structure Ti_3C_2, a new class of 2D layered materials (MXenes) consists of carbon nitrides, nitrides, and transition metal carbides. This has led to its wide interest by researchers in many fields. The general formula for MXenes is $Mn^{+1}XnT_x$ ($n = 1$–4), where M is the transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, and Mo), X is carbon and/or nitrogen, and T_x is the surface termination. The most commonly used preparation method for MXenes is selective wet etching from layered precursors, followed by layering. The structure of MXenes could be tuned by different strategies during etching and layering to achieve the desired properties and functions. Take the most basic MXenes-Ti_3C_2 as an example. Ti–Al bonds are weaker than Ti–C bonds, so Ti–Al bonds are more likely to break under vacuum, heating, or molten metal, which can be selectively removed from its corresponding MAX stage. The Al layer was etched to obtain Ti_3C_2. Moreover, the

Ti_3C_2 obtained by this route not only retained the hexagonal tightly packed structure of the original Ti_3–AlC_2 MAX phase but also stacked alternately in two C atomic layers as well as three Ti atomic layers. The interlayer is connected by Ti–C bonds with mixed covalent–ionic–metal characters. The conductive layered structure, large specific surface area, and tunable surface properties of MXenes make it excellent in applications such as catalysis performance, sensing, and energy storage. For example, a laboratory successfully prepared a truncated octahedral bipyramidal TiO_2 (TOB–T)–MXenes Ti_3C_2 composite photocatalyst using a simple one-step calcination method. During the calcination process, the fluorine concentration dropped sharply, which greatly reduced the toxicity of the samples and significantly improved the conductivity of the samples. Moreover, calcination not only did not destroy the original 2D multilayer structure of the material but also established abundant heterointerfaces between the (101) and (001) crystal planes, which prevented the recombination of photogenerated carriers in TiO_2 and improved the photocatalytic hydrogen production activity.

15.3.2 Applications of Agro-waste-Based Nanoparticles in Medicine

15.3.2.1 CNMs as Drug/Gene Carrier

Drug Carrier

The unique nanotube diameter and hollow structure of CNTs facilitate the accommodation of biologically specific molecules or drugs. However, its application in biomedicine is limited due to its insolubility in any solvent. According to this shortage, modifying its surface to improve its water solubility, biocompatibility, and targeting has become a very hot research field. It has been reported that by modifying single-walled CNTs and attaching folic acid to their surface, folic acid receptor-positive tumor cells can be targeted. However, normal cells will not be adversely affected. Previous research synthesized CNTs modified with polyethylene glycol (PEG) as a carrier for the anticancer drug paclitaxel (Alagarsamy et al. 2021). The results of the study showed that compared with CNTs and paclitaxel, the nanotube-loaded drug can improve the penetration of the drug and residence time in the blood circulation and has a good inhibitory effect on the growth of tumors. Some study used single-walled carbon nanotubes (SWCNTs) as a carrier, labeled integrin $\alpha v\beta 3$ monoclonal antibody as a tumor-targeting molecule on SWCNTs, and constructed a new tumor-targeting probe based on CNTs. The $\alpha v\beta 3$ human brain glioma cell U87MG was used as a model for research, and the results showed that this new material has good targeting to U87MG to make it as a potential tumor-targeting drug carrier.

Gene Carrier

Gene therapy is an emerging research field at present, which is a method for specific treatment of diseases by sending target genes into target cells to replicate and express. The implementation of gene therapy required a suitable gene carrier to protect DNA from being degraded by nucleases. Therefore, finding a suitable gene carrier is the main direction of current gene therapy research. CNTs have achieved great success in gene transfection. In 2004, a study reported a carbon–nanotube-transfected β-gene at the first time. For example, positively charged aminated MWCNTs were found to have high transfection rates. Subsequently, the study of CNTs in gene transfection was initiated. Sargazi et al. (2022) modified CNTs with polyethylenimine (PEI), and the transfection efficiency was three times that of PEI. Aminated CNTs could be transfected into HUVECs and human melanoma cell line A375 by a plasmid carrying a green fluorescent protein (green fluorescent protein, GFP) reporter gene. When the charge ratio of the plasmid is 10:2, the transfection efficiency is the highest (Sargazi et al. 2022). Another study injected the telomerase reverse-transcriptase (TERT) gene into tumor-bearing mice using SWCNTs as a carrier, and the tumor growth was also well inhibited.

15.3.2.2 Applications of CNMs in Bioimaging

Bioimaging Agent

Organisms basically do not produce fluorescence in the near-infrared region. Due to the unique structure of SWNTs, strong fluorescence could be generated without modification by the high-resistance quenching and photobleaching of fluorophores. Therefore, researchers have studied the application of CNTs in imaging. It has been reported that after SWCNTs enter cells, their own Raman spectral signals and fluorescence signals can be retained for up to 3 months in the process of normal cell division, proliferation, and differentiation. This kind of feature can be used as a biomarker for long-term follow-up observation. The DNA-wrapped CNT–iron oxide complex was synthesized, which has dual functions of magnetic resonance imaging and near-infrared fluorescence. Cells treated with this material not only have magnetic resonance imaging (MRI) signals but also use CNTs in the near-infrared region. Fluorescence can also clearly observe the boundaries of cells (Mamidi et al. 2022).

At present, some progress has been made in the application of GO in biological imaging by using the optical properties of graphene. A study used the intrinsic fluorescence of GO in the near-infrared spectral region for the first time to study the endocytosis of chemical drugs loaded with GO. Since then, research has studied the rGO grafted with fluorescent dye-labeled gelatin in fine applications in cellular imaging and drug delivery capabilities. Recently, some researchers explored the possibility of applying graphene quantum dots (GODs) to cell imaging. The results showed that GODs have better biocompatibility and physiological stability than CdSe quantum dots that are commonly used at present. Due to the advantages of low toxicity, it is promising to be directly used for intracellular imaging.

MRI Agents

The clinical MRI contrast agents are mainly chelates formed by highly paramagnetic metals and ligands, mainly La-containing metal complexes, among which diethylenetriaminepentaacetic acid (DTPA) is the most widely used. The current research on MRI agents is mainly based on Gd-based compounds. Some study used 2-azide alcohol to hydroxylate multiwalled CNTs and grafted hyperbranched polymeric glycerol on its surface to improve its dispersion. A large number of reaction sites was used to connect diethylene. Gadolinium triamine pentaacetate and CNTs that have large specific surface area are used to adsorb hyaluronic acid (HA), a lymphotropic biomacromolecule, through covalent bonds. The results showed that this material can more accurately determine the lymphedema model. Existing research results showed that after the metal is chelated, the relaxation ability is reduced because the tissue specificity is not strong. It is easy to release toxic metal ions, causing damage to the body. The emergence of intercalated metallofullerenes brings hope to solve this problem. First, the metal atoms are protected by carbon cages formed by C atoms and will not be released. In addition, tissue specificity and biocompatibility could be enhanced through different functional modifications of the carbon cages. Studies have shown that intercalated metallofullerenes have the potential to become a new generation of MRI agents.

15.3.2.3 Applications in Cardiovascular Therapy

Cardiovascular disease (CVD) is the deadliest disease in the world. According to the “China Cardiovascular Health and Disease Report 2020,” in 2018, the mortality rate of CVD in rural China is 46.66%, and that of urban residents was 43.81%, higher than tumors and other diseases. In the past 20 years, the potential application value of carbon NMs (i.e., CNTs, fullerenes, graphene, nanodiamonds, and their derivatives) in the field of biomedicine has set off a research boom (Alagarsamy et al. 2021).

Drug/Biomolecule Delivery

The new nano-drug delivery system solves the problems of traditional methods such as poor bioavailability, high drug toxicity, lack of targeting, and frequent administration. The advantages of CNMs, such as small particle size, high specific surface area, excellent drug loading, and easy surface functionalization, make CNMs an effective nano-drug/gene drug delivery tool. Because the drug-carrying capacity of pristine graphene is limited, GO and rGO have become the preferred carriers at present. After functionalization, toxicity targeting and sustained release of graphene are well improved. Some research loaded irbesartan onto a conductive polymer film composed of rGO, HA, gelatin, and polyethylene oxide, which could effectively control the release of the drug. Vascular endothelial growth factors (VEGF) can induce angiogenesis in ischemic myocardium. A study combined polyethyleneimine-functionalized GO with VEGF-165 angiogenic gene (DNAVEGF) into a nonviral gene delivery system (fGOVEGF) and incorporated it into a low-modulus gelatin methacrylate. GelMA hydrogel for local gene therapy of acute myocardial infarction (AMI). The myocardial capillary density in the peri-infarct area of AMI rats in the fGOVEGF/GelMA group was significantly increased, and the scar area was reduced, indicating that the fGOVEGF/GelMA gene therapy system is feasible for ischemic heart disease.

Biological Sensor

Biosensors could detect cardiac biomarkers early and continuously monitor CVDs in order to protect and treat cardiac function in time. CNMs are ideal materials for CVD diagnostic biosensors because of their small size, large specific surface area, low cost, and excellently electrical and optical properties. During AMI, creatine kinase, myoglobin, cardiac troponin (cTn), and brain natriuretic peptide markers are released from dying cardiomyocytes. Stable and sensitive detection of these markers is the key issue to the early diagnosis of CVD. Some researchers prepared a hydrochloric acid-modified ultrasensitive graphite paper electrode and functionalized it with a cardiac troponin T (cTnT) antibody to detect cTnT levels in human serum down to the subfemtosecond level. Owing to fast charge transfer kinetics, excellent mechanical stiffness, and outstanding electrocatalytic activity, metal and nanometal chalcogenides are ideal materials for doped or functionalized graphene electrodes to enhance the detection selectivity and sensitivity of cardiac biomarkers. In this study, metal chalcogenides (molybdenum selenide, nMo_3Se_4) and rGO were embedded in indium tin oxide-coated glass electrodes and functionalized with bovine serum albumin to detect cardiac troponin L (cTnI), which is more efficient than the commonly used zirconia electrode. Sensitivity increased by nine times. Sensitivity to cardiac biomarkers could be improved by attaching bioactive molecules to the CNT surface. Different CNM biosensors have unique properties. All electrodes showed good sensitivity and selection signals for biomarkers, with the SWCNT-based biosensor showing the most outstanding overall performance. In the future, in-depth research on the mechanism of CNM-mediated CVD diagnosis is required in order to provide the best commercial products for the diagnosis and treatment of CVD.

15.3.3 Applications of Agro-waste-Based Nanoparticle Aviation Sector

The development of aviation technology is closely related to the development of aviation materials, which was an important factor affecting the development of modern advanced technology and industry. With the development of science and technology, modern aviation technology has put forward higher requirements for aviation materials, including lightweight, functional, and intelligent structures. The demand for lightweight materials is a powerful means to reduce fuel consumption and aviation emissions and to greatly improve the performance of fighter aircraft. Functional requirements for radar, fire control, and stealth also require materials with excellent optical, electrical, thermal, and magnetic properties. In addition, intelligent responsive materials are an important development direction of the modern aviation industry. Different from traditional metal materials, the application of composite materials can well meet these needs. In the 1970s, composites are used in only 1–3% of civil aircraft. Today, the use of composite materials in Boeing 787 is already as high as 50%, far exceeding the 20% for aluminum. Compared with aluminum alloys, composites are lighter, stronger, tougher, and more resistant to fatigue and corrosion defects and offer lower maintenance costs, longer fatigue life, lower thermal expansion, and higher functional design ability (Lu et al. 2022).

15.3.3.1 Research Status of CNM-Reinforced Structural Composites

Structural materials are mainly used in the structural parts of aircraft to withstand static loads caused by their own weight and various dynamic loads generated in flight, such as fuselage, wings, drive shafts, and engines. On the premise of meeting the same load-bearing requirements, the lightweight of materials has always been an eternal theme pursued by the aviation industry. The reduction of aircraft weight can effectively reduce fuel consumption and emissions and improve the performance of fighter aircraft. Carbon NMs represented by CNTs and graphene have excellent mechanical properties, and the nanocarbon composite materials prepared as reinforcements can usually have excellent mechanical properties under the premise of ensuring light weight. In the initial research stage of nanocarbon-reinforced structural composites, limited by inadequate characterization and synthesis methods, most of the work focused on dispersing nanocarbon powders directly in the matrix as reinforcements. However, carbon NMs usually "agglomerate" in the matrix under the action of surface energy, and it is difficult to disperse uniformly in the matrix, which greatly limits the maximum performance of carbon nanocomposites. Researchers have made significant breakthroughs in solving the trouble of nanocarbon "agglomeration" by designing the architecture of nanocarbons in composite materials. According to the different design of nanocarbon architecture, it can be divided into three categories (Fig. 15.6).

Layered Stack Structure

The single-walled CNT film is used as a sheet to prepare resin-based carbon nanocomposites using a "layer-by-layer assembly" method. This structural design can not only significantly reduce the agglomeration effect of single-walled CNTs but also achieve a higher surface area. Internal stiffness, tensile strength of 40.97 MPa, Young's modulus of 1.13 GPa, and toughness of 3.11 MJ m^{-3}, which are 93.53%, 59.15%, and 146.83% higher than pure epoxy resin, respectively, mainly due to carbon. The high stress transfer efficiency between CNTs in the nanotube film, compared with the traditional CNTs uniformly dispersed reinforced composites, this stacked structure design can achieve higher efficiency when using less CNTs. High mechanical reinforcement effect.

Directed Structures

The second category is directed structures. This structure solves the lack of load transfer efficiency caused by the bending of the reinforcement and at the same time overcomes the problem of nanocarbon aggregation created by the interactive van der Waals force, a kind of ideal structure for building high-strength composites. The design of the oriented structure can be achieved in three ways, first by direct-oriented growth of nanocarbon macrobodies and then by infiltrating the matrix into them. Some studies infiltrated epoxy resin in oriented CNTs. Under the action of CNTs, the electrical and mechanical properties of the composite were significantly enhanced,

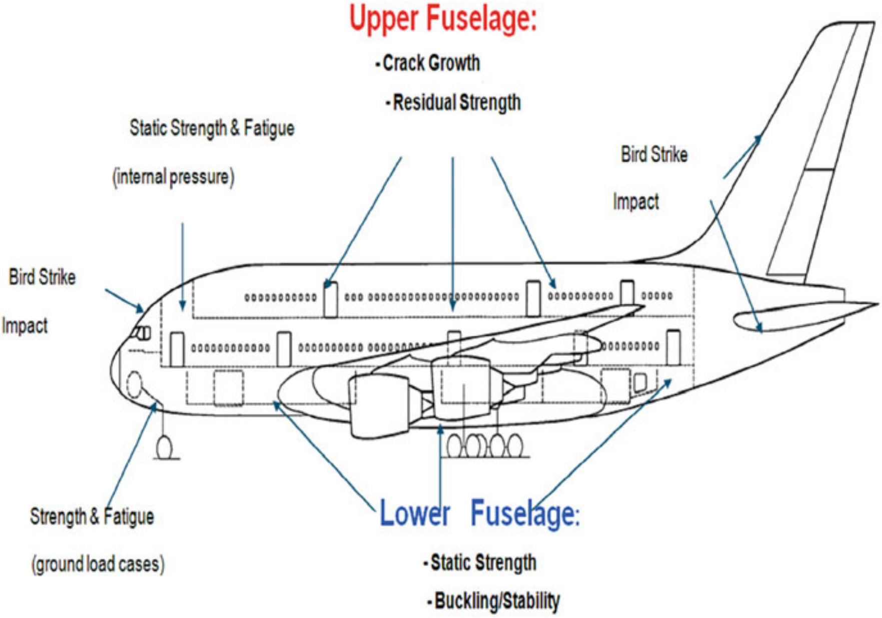


Fig. 15.6 Place where nanomaterials can be used in aircraft (Kumar and Dhanasekaran 2019)

and the volume percentage of the prepared CNTs was 16.5%. The composite has Young's modulus of 20.4 GPa and a tensile strength of up to 231.5 MPa. The third category is the network structure. The network structure is a collaborative design based on the orientation and distribution of carbon NMs. Low CNT content has the potential to achieve outstanding mechanical properties in all directions, showing a broad application prospect in the fabrication of lightweight composites with isotropic mechanical properties. Construction of the network can be achieved using the template and self-assembly methods.

3D Network

Epoxy resin was injected into graphene three-dimensional network to achieve the purpose of constructing carbon nanocomposites. Graphene 3D network to construct nanocarbon composites. Under external load, the graphene network can act as crack tip passivation and prevent crack propagation, which enables the nanocarbon composite to have 1.78 MPa with improved modulus and strength compared with pure epoxy resin. In terms of the self-assembly method, some researchers revolved a self-assembled CNT into a 3D network of CNTs (CNT sponge) using the CVD method, and the density can be 5–25 mg. The as-prepared CNT macrobodies exhibit excellent compression and recovery properties, with volume shrinkage as high as 90%, and the ability to recover most of the volume by free expansion.

15.3.3.2 Research Status of CNMs in the Field of Electromagnetic Shielding

Electromagnetic radiation often interferes with electronic equipment (such as electronics, radar, and wireless communication equipment), causing the equipment to operate abnormally. In order to protect electronic components and prolong the service life of key electronic equipment of spacecraft, electromagnetic shielding materials have increasingly attracted researchers' attention. The ability of a material to shield electromagnetic waves is related to its inherent electrical conductivity; however, most polymers are insulating and cannot shield electromagnetic waves. Therefore, introducing carbon nanofillers into polymers is an excellent way to fabricate composites with strong electromagnetic shielding capabilities. Among the many conductive fillers, carbon black is widely applied in the synthesis of nanocarbon composites for electromagnetic shielding due to its low cost. The electromagnetic shielding and conductivity properties of the composites become stronger by adding an appropriate amount of carbon black to the polymer matrix. In order to obtain excellent electrical conductivity and electromagnetic shielding properties of the material, higher filler loadings are often required. This could lead to agglomeration of fillers that reduces the mechanical properties of the composite necessary in polymers. In a previous study, a composite material was prepared with carbon black as the conductive filler and a water-insoluble polymer blend as the matrix. Using ethylene methyl acrylate and ethylene octane copolymer as blend polymerization, the double-permeation phenomenon is realized in the composite material. The selective distribution of carbon black in different polymers significantly improves the electrical conductivity and shielding properties of the composite materials (31.4 dB). CNTs have excellent mechanical and electrical properties as well as high aspect ratios and also have broad application prospects in the field of electromagnetic shielding. An electromagnetic shielding composites composed of single-walled CNTs and polyurethane was prepared through a simple physical mixing process. The electromagnetic shielding properties of the composites in the X-band is 16–17 dB. Although study finds that improved carbon nanotubes and the content of the tube can improve the electromagnetic shielding properties of the material, agglomeration of CNTs also increases the difficulty of material preparation. Hu et al. prepared a multifunctional aerogel film composed of strong aramid nanofibers, CNTs, and hydrophobic fluorocarbon resin using the blade coating method and freeze-drying process. High conductivity, outstanding hydrophobicity, and large specific surface area enable composites to be effective at electromagnetic shielding in the X-band to 54.4 dB.

15.4 Application of Nanomaterials From Agricultural Waste for Agricultural Wastewater Treatment

Agricultural water pollution from agricultural activities and industrial production is a major concern today. A variety of contaminants entering the aquatic environment pose serious threats to ecosystems and humans. Agricultural wastewater mainly comes from agricultural product processing wastewater, crop irrigation wastewater, and livestock as well as poultry breeding wastewater (Wei et al. 2018). There are a large number of organic pollutants in agricultural processing wastewater. In addition, there are a large number of pesticide residues in crop irrigation wastewater. And livestock and poultry farming wastewater contains a variety of toxic metals, antibiotics, and residual veterinary drugs (Wei et al. 2018). The current treatment methods for agricultural wastewater include biodegradation, advanced oxidation, physical adsorption, etc. But the previous means of treating agricultural wastewater usually had many drawbacks (i.e., difficult to operate, expensive, inefficient, and the by-products of degradation are still toxic). Therefore, a novelty, efficient, and environment-friendly treatment method is urgently needed. The use of biodegradable, low-cost, available agroindustrial biowaste to produce bio-nanosorbents, bio-nanocatalysts, and bio-nanodisinfectants for wastewater treatment provides an excellent avenue for environmental protection (Shah and Aziz 2020). CNTs, CNFs, GO, ACs/BCs, and nanocellulose have all been discovered and put into the treatment of agricultural wastewater. All these materials could be made from AWs and provide excellent treatment performance for wastewater. In this section, various examples of the aforementioned NMs in the treatment of hazardous substances in agricultural wastewater would be illustrated.

15.4.1 Carbon Nanotubes

A study on poultry manure as a material for the synthesis of CNTs has been conducted (Liu et al. 2008). In the study, poultry manure was used as a source of hydrocarbons for the production CNTs. The Ni/Mo/MgO molar ratio was optimized using the response surface methodology. Among them, Ni was found to have the highest ratio compared with Mo and MgO. Poultry manure was combusted as a source of hydrocarbons in the presence of a Ni/Mo/MgO catalyst in an electrically heated tube furnace to produce CNTs. High yields of CNTs were prepared using optimized molar ratio (Ni/Mo/MgO (4:0.2:1) catalytic precursors at 825 °C, 100-mg catalyst weight, 4-g poultry litter weight, and 12-min burn time.

The excellent physicochemical properties of CNTs (i.e., excellent electrical conductivity, excellent chemical inertness, strong mechanical strength, good water transport performance, low density, high specific surface area, small volume, hollow structure, high porosity, and controlled pore-size distribution) determine their wide application in the water treatment industry (Liu et al. 2008). As for wastewater discharged from agricultural activities, there have been numerous examples of CNTs being used to remove a wide range of environmental pollutants (i.e., organic substances, pesticides, pharmaceuticals, antibiotics, and inorganic ions) (Jain et al. 2022). The adsorption of CNTs is very effective for the purification of water bodies, and a treatment of pig farm wastewater showed that CNTs demonstrated objective adsorption efficiency for eutrophic water bodies (Liu et al. 2008). Studies have also shown that the adsorption of organic pesticides on CNTs depends on charge-transfer interactions, hydrophobic interactions, π–π interactions, and electrostatic interactions. It was concluded that the hexagonal arrangement of carbon atoms and compatible pore size in CNTs provide a very favorable interaction between CNTs and pesticides. Conversely, in addition to the various characteristics of CNTs, the geometry of different types of pesticides also affects the degree of adsorption of CNTs. This implies that contaminant molecules with a planar structure exhibit stronger adsorption than those with a nonplanar structure (Abbo et al. 2021). Multiwalled carbon nanotubes (MWCNTs) are a type of CNTs, and some studies have used MWCNTs to remove diazinon pesticide residues from agricultural production wastewater (Dehghani et al. 2019). The adsorption studies of MWCNTs on diazinon were carried out in a batch reactor. The experiments were performed at room temperature (24 ± 2 °C). The adsorption mechanism of MWCNTs on diazinon was comprehensively evaluated by setting different pH values (4 and 7), contact times (1, 5, 8, 10, 12, and 15 min), different initial concentrations of diazinon (0.3, 0.5, and 1 mg L^{-1}), and different amounts of MWCNT doses (0.1 and 0.3 g L^{-1}). The results showed that MWCNTs exhibited extremely high diazinon removal efficiency (98%) at a contact time of 15 min, an adsorbent dose of 0.1 g L^{-1}, an ambient temperature of 24 ± 2 °C, and an initial diazinon concentration of 0.3 mg L^{-1}. Overall, MWCNTs have great potential for the removal of organophosphorus pesticides from water.

15.4.2 Carbon Nanofibers

ACs are one of the carbon materials widely used in adsorbents and catalyst supports. AWs (i.e., wheat straw and nut shells) could be used for producing ACs. Hollow carbon nanofibers (HCNFs) were discovered during microwave pyrolysis of palm kernel shells (PKS) at 500 °C and 600 °C (Wu et al. 2016). In the study, PKS successfully produced HCNF on the surface of BC during microwave pyrolysis at 500 °C and 600 °C. SEM exhibited that HCNFs are not formed during conventional fixed-bed pyrolysis, indicating that microwaves are important in the formation and fabrication of HCNFs. The yield of HCNFs increased with increasing microwave pyrolysis temperature. HRTEM analysis revealed that HCNF had a multiwalled structure with a graphitic interlayer spacing of 0.34 nm. The XRD analysis of HCNF revealed two distinct peaks at $2\theta = 26.3°$ and $43.2°$, corresponding to the graphitic structure of HCNF. The half-full width of the very narrow $2\theta = 26.3°$ peak of the microwave BCs prepared at 600 °C indicated excellent crystallinity of HCNFs. The ID/IG intensity ratio in the Raman spectrum of microwave pyrolyzed BC decreased at 600 °C, indicating that the carbon order in HCNF increased with increasing pyrolysis temperature.

Currently, CNFs have been widely used in water purifiers, especially silver-carrying CNFs with dual functions of adsorption and sterilization. For the treatment of wastewater generated from agricultural production, CNFs have also shown excellent adsorption performance. It has been shown that when CNFs cross each other in their pristine state, they are mostly mesoporous (2–50 nm) and suitable for adsorption of organic pollutants with larger molecular weights. On the contrary, CNFs obtained after surface treatment have micropores (1–2 nm) and are suitable for adsorbing smaller inorganic contaminants. The large surface area, multiple surface sites, and high porosity of CNFs contribute to its suitability for acting as good adsorbents for pollutants. The surface of CNFs can be easily functionalized by chemical modification, making them selective adsorbents. A novel eco-friendly Ag–Cu/CNF nanocomposite was investigated for the removal of hazardous rhodamine B dye and pesticide 2,4-D (Saharan et al. 2021). The adsorption isotherm experiments showed that the results were best fitted by the Langmuir model due to monolayer adsorption. In addition, the synthesized sorbent was able to remove more than 80% of RhB and 2,4-D from spiked water samples. The adsorption evaluation experiments showed that the best results were achieved by invading the ultrasound-assisted adsorption due to the enhanced mass transfer of the adsorbent in the available pores of the Ag–Cu/CNF surface and the fabricated nanocomposite surface.

15.4.3 Graphene

Graphene has attracted the attention of the industry for its outstanding gas impermeability, mechanical properties, superconductivity, high thermal conductivity, and large specific surface area (Kabiri et al. 2017). It was shown that 1D graphene fibers with novel structures were prepared by heat treatment of rice husk, a natural by-product containing high amounts of silica (Fujisawa et al. 2019). In the study, 10 g of natural flake graphite was dried in a vacuum oven at 80 °C for 24 h, mixed with an acid composed of concentrated nitric acid (50 mL) as well as concentrated sulfuric acid (200 mL), and then intercalated for 24 h to form a blue graphite intercalation compound (GIC). Sulfuric and nitric acids were used as oxidizing agent and intercalating agent, respectively. The mixture was filtered and carefully washed with deionized water until the pH of the solution reached 6. After drying in a vacuum oven at 80 °C for 24 h, expanded graphite (EG) was generated by rapid expansion of GIC in a muffle furnace at 105 °C for 15 s. EG was further treated with microwave, and the resulting fluffy powder was named microwave expanded graphite (MEG). MEG (3 mg mL^{-1}) was dispersed and stripped in (500 mL) DMF at 6000 rpm for 60 min with 5-min intervals. The resulting nanoparticles were dried with MW radiation and further characterized. The results of the study showed that almost all AWS materials were converted to graphene nanoparticles. This simple graphene synthesis method offers a new cost-effective way for bulk and etch-free standalone graphene applications. It also enables the reuse of AW in wastewater treatment. Graphene-based NMs are recognized as effective adsorbents for removing contaminants in wastewater from various sources. Among the various types of carbon NMs, 2D graphene, GO, and reduced graphene (rGO) have been found to be as efficient as CNTs in wastewater treatment. The outstanding advantages of graphene, GO, and rGO are mainly due to high selectivity, presence of abundant active sites, and large surface area (Abbo et al. 2021). Like CNTs, graphene and its derivatives have strong chemical stability and high surface area-to-weight ratio

(2600 m^2 g^{-1}), which drives them as potential adsorbents for the elimination of toxic metal ions and organic contaminants from domestic and agricultural wastewater.

15.4.4 Activated Carbon

ACs have been well developed in the field of pollutant adsorption. It was also found that there are many ways to produce ACs from AWs. for example, ACs are prepared from AWs by microwave-assisted chemical reagent activation. In addition, ACs can be produced by thermal processing of rice husks. The use of ACs for water treatment is an effective technology compared with conventional adsorbent technology because it is readily available, simple in design and operation, and effective in removing persistent dyes and pollutants from wastewater. The adsorption of pollutants by ACs is divided into two types: chemisorption and physical adsorption. The distinction between these two types of adsorption stems from the type of interaction between ACs and the different types of adsorbents. Chemisorption is classified according to chemical interactions with the exchange of electrons between two phases, leading to irreversible processes and the formation of permanent bonds. But physical adsorption involves Vander der Waals interactions, π–π interactions, and electrostatic or H–bonds, leading to a reversible process. ACs are currently used in the field of treating all types of wastewaters. For example, when using AC to treat industrial wastewater, its adsorption effect can be used to remove organic components, heavy metal ions, grease, and residual disinfectants (Seifi et al. 2020). When using ACs to treat domestic wastewater, it can remove harmful substances from the water and remove the taste and smell of the wastewater. It is also able to disinfect the water in bacteria and viruses. In particular, ACs could absorb a variety of organic pollutants, pesticides, etc. when treating agricultural wastewater.

Some study evaluated the adsorption capacity of ACs on wastewater containing some pollutants from agricultural production (i.e., 2,4-dichlorophenoxyacetic acid (2,4-D), atrazine) (Chang et al. 2022). The study applied the pore volume and surface diffusion model (PVSDM) and external mass transfer mode (EMTM) for predicting the kinetic profiles. Through batch adsorption tests, it was found that the optimum adsorbent dosage of 1 g L^{-1} resulted in 82% and 95% removal of 2,4-D and atrazine, respectively. The equilibrium data for 2,4-D and atrazine were precisely fitted by the Langmuir and Freundlich isotherm models, respectively. The thermodynamic fitting parameters indicated that the adsorption is enthalpy-controlled, exothermic, and favorable. External mass transfer was the rate-limiting mechanism for atrazine adsorption on ACs ($Bi < 0.1$), whereas 2,4-D adsorption on ACs (Bi: 3.82–4.52) was controlled by both surface diffusion and external mass transfer. ACs showed excellent efficiency in the treatment of agricultural wastewater, achieving 84% and 83% removal of atrazine and 2,4-D, respectively. The experimental results showed that the adsorption and removal of atrazine (95%) was much higher than that of 2,4-D (82%) at an optimum adsorbent dosage of 1 g L^{-1}. The higher affinity of AC to atrazine may be due to the interaction between the N-heterocyclic structure of atrazine and the active sites of ACs. The Freundlich and Langmuir isotherm models were adapted to fit the adsorption curves of atrazine and 2,4-D on ACs, respectively. The isothermal and thermodynamic results indicated that adsorption was enthalpy-controlled, exothermic, and favorable. ACs also effectively treated agricultural wastewater.

Also, previous study converted PKS into ACs by microwave pyrolysis combined with steam activation and used the ACs made by this method to remove herbicides from agricultural wastewater with very remarkable results (Lam et al. 2019). The adsorption efficiencies of BCs 700 and ACs 30 obtained by this pyrolysis method were examined for 2,4-D herbicide at certain doses (10, 20, 30, 40, and 50 mg) and under adsorption temperatures (30, 40, and 50 °C). The adsorption efficiency of ACs on 2,4-D was found to be higher (11 mg 2,4-D g^{-1} AC) than that of BC (7 mg 2,4-D g^{-1} BC). The adsorption efficiency of BC and AC was affected by temperature and dosage. Increasing the dose from 10 to 50 mg would enhance the adsorption efficiency from 1 to 7 mg g^{-1} for BCs and 3 to 11 mg/g for 2,4-D for ACs, respectively. The more remarkable adsorption efficiency could be attributed to the higher surface area resulting in an increase in available adsorption sites after using a higher dose of ACs. The adsorption efficiency of 2,4-D enhanced slightly with the increase in temperature. As the temperature increased from 30 to 50 °C, the uptake of 2,4-D by BCs increased from 1.98 to 2.31 mg g^{-1}, and the uptake of 2,4-D by ACs increased from 4.62 to 5.00 mg g^{-1}. A highly porous AC of 83 wt% was obtained with a surface area of 419 m^2 g^{-1}. The ACs at 11 mg of 2,4-D g^{-1} showed the highest adsorption efficiency. Pyrolysis holds great promise for the preparation of ACs as an adsorbent that can also be used to remove herbicides from contaminated agricultural surface water.

15.4.5 Nanocellulose

Nanocellulose has excellent physical and chemical properties. Especially because of the presence of hydroxyl groups, many studies have shown that nanocelluloses could be used in many fields such as textiles, food packaging, water purification, etc. (Nehra and Chauhan 2022). The feasibility of nanocellulose as a base material is due to the large specific surface area and abundant hydroxyl functional groups. These abundant hydroxyl groups exhibit strong attraction to contaminants carrying ionic structures or dyes and could be easily modified to significantly improve the adsorption capacity of nanocellulose. Various forms of nanocellulose (bacterial cellulose, CNFs, and cellulose nanocrystals) have been used in wastewater treatment, including membranes and filters (e.g., nanoparticle filtration or affinity membranes) and adsorbents for some contaminants (e.g., nitrates, dyes, and heavy metal ions) (Mautner 2020).

The application of nanocellulose in the treatment of contaminated water could be achieved using various methods. One of the most direct methods is to use nanocellulose for direct adsorption. The adsorption process refers to the attachment of contaminants such as dyes or heavy metal ions to the surface of the adsorbent through physical and chemical interactions. The key to the success of this process is the high specific surface area and availability of adsorption sites. Thus a large number of contaminants in the aquatic environment could be removed, especially cations such as heavy metal ions. In addition, through appropriate modification of the adsorbent, it is also possible to remove negatively charged ammonium groups such as nitrate or phosphate, as well as organic pollutants, including oils, dyes, pharmaceuticals, and pesticides. Even though heavy metal ions and dyes are attracted by hydroxyl groups, modifying hydroxyl groups into functional groups with higher affinity for charged groups can greatly improve the adsorption capacity. The CNCs prepared by sulfuric acid or phosphoric acid hydrolysis have anionic groups, so they have strong adsorption affinity for heavy metal ions and dyes. In addition to these naturally and inherently occurring functional groups, there are various possibilities to attach other functional groups similar to those commonly used in ion-exchange resins. Several reviews have recently summarized the use of modified nanocellulose and its affinity for contaminants (Mautner 2020). Another option for the use of nanocellulose in water treatment operations is flocculation, a method of removing suspended particles or compounds present in wastewater through aggregation of colloidal particles usually caused by electrostatic interactions. In addition, nanocellulose has been found to act as a carrier for antimicrobial NPs or catalysts, such as zero-valent iron and Pd or TiO_2 NPs, capable of catalyzing the degradation of dyes or organic contaminants. Separation of oil from water by cellulose-based NPs is a more important task. Nanocellulose-based photocatalysts have been reported as environmentally friendly alternatives to synthetic materials as substrates for photocatalytic destruction of contaminants (Mautner 2020).

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Agricultural Waste as a Source of Fine Chemicals

16

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Abstract

In the modern scenario, an exercise of agricultural waste resources to swap petroleum-based products as a major feedstock for fine chemicals, liquid fuels, and intermediate materials has become a source of concern in most of the world's regions. It is stimulating as a result of rising petroleum-based product prices, the negative environmental effects of petroleum-based feed, and the benefits of renewable resources, such as their sustainability and abundance. This chapter discusses the chemical composition of agricultural waste and the possibilities for fine chemicals and related products made from agricultural waste resources. Carbohydrates and lipids, which account for roughly 95% of biomass produced annually, are widely used as best feedstocks for fine products and specialty or organic chemicals. The conversion routes, including direct refining, chemical and biochemical routes, and selected technological advancements, are also discussed. Besides, selected waste biomass sources, biochemicals, biomass conversion pathways, derivatives, and potential applications are elaborately discussed.

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Agricultural waste · Fine chemicals · Sustainable resources · Biorefinery · Conversion technologies

16.1 Introduction

Globally, a lot of agricultural wastes (AWs) are generated every day to satisfy the increasing demands of the rapidly expanding population (Jayakumar et al. 2023; Awogbemi and Kallon 2022). Improper management and abandonment of agri-waste unenthusiastically affect the atmosphere and deteriorate human health, while inadequate consideration has been made to address this problem (Sadh et al. 2018). Agricultural residues are not always readily available in all areas and places. Crop waste, food processing waste, livestock waste, and animal waste are the major categories of these wastes (Jayakumar et al. 2022; Amran et al. 2021). Recently, the process of converting agricultural wastes into useful by-products for a choice of industrial supplements like materials, medicine, and packaging of food has gained enormous interest. This waste management approach is considered economical, environmentally beneficial, and long-lasting (Hodaifa et al. 2019). Agricultural waste does not properly manage, adds no value, and instead affects the environment and costs financially. In contrast, petroleum feedstock covers only narrow functionality, but the agri-waste biomass restrains extra functionality, similar to use as fuels and chemicals, and the major dispute in this ground is to find strategies extended to direct the functionality in an absolute product (Gundupalli et al. 2022). Agri-waste usage will support climate change mitigation, develop innovative biodegradable and bio-ingredient materials, and promote green intensification and a globular bio-wealth.

A major agricultural waste described as lignocellulosic biomass contains complex molecular structures, including cellulose range of 35 to 55, hemicellulose range of 20 to 40, and lignin range of 10 to 25 (by weight %). Possible extracts such as resins, lipids, terpenes, flavonoid, and fat components are also present in lesser magnitude (Rowan et al. 2022). In general, a widespread natural polymer of linear carbohydrates that contains D-glucose is cellulose. Hemicellulose is less resistant to chemicals, rapidly dissolved by weak bases, acids, and enzymes, and is amorphous (Awogbemi and Kallon 2022). On the other hand, lignin is a complex and recalcitrant phenolic macromolecule composed of phenyl propane-type units. It is defiant to microbial assail and can prohibit water from damaging the matrix of polysaccharide-protein on plant cells because of an extremely asymmetrical polymeric structure (Xu et al. 2014). In contrast, cellulose could be hydrolyzed to form simple sugar and then turn out into highly valuable chemicals and fuels by fermentation. However, small crystalline than cellulose and hemicellulose is nonetheless utilized to produce valuable industrial chemicals and other supplementary significant products (Awogbemi and Kallon 2022). There are numerous fine chemicals that can be produced from agri-waste like glucose, proteins, peptides, triglycerides, glycerols, steroids, amino acids, biocides, alkaloids, etc. Even though the conventional way of managing agricultural waste has been to simply discharge it into the environment, whether it has been treated or not, this method involves six main functions: production, collection, storage, treatment, transport, and utilization. Among various technologies utilized for agricultural waste management, the most profitable and sustainable conversion techniques are physical, chemical, and biochemical conversion tools that are common to manage this waste (Capanoglu et al. 2022). Physical conversion tools relate to the processing and modification of biomass to generate highly valuable products, thus recognizing the value-added exploitation of lignocellulosic waste materials. On the other hand, gasification, carbonation, combustion, hydrothermal liquefaction, and thermal decomposition technologies are included under chemical conversion technologies (Outline 2017). Biochemical conversion involves the application of enzymes from bacteria or other microorganisms to decompose biomass at ambient temperature and pressure using anaerobic digestion, fermentation, or composting. This conversion technology requires physical, chemical, and biological pretreatments to convert biomass into an appropriate and useful product. The crucial divergence among the physical and chemical tools of conversion processes is that pretreatments in biochemical conversion technologies of biomass strive to accomplish supreme conversion effects rather than producing end products. Biochemical processes have the advantage of low processing temperature and good product selectivity compared to other conversion technologies. However, they typically involve excessive processing durations, inadequate space-time, and preprocessing steps (Gundupalli et al. 2022).

16.1.1 Potential Use of Agri-Waste Sources

Agricultural wastes can be utilized to generate value-added sustainable final products of fine chemicals, antioxidants, nutraceuticals, bioactives, biopeptides, biopolymers, and antibiotics. Peels from fruits and vegetables are a significant source of agricultural waste that can be converted to a variety of fine chemicals, such as pharmaceutical products (Sadh et al. 2018). Moreover, these wastes are the main sources of compounds with anti-inflammatory, antioxidative, anti-allergenic, and antimicrobial qualities, including polysaccharides, dietary fiber, phytochemicals, protein, and flavor (Amran et al. 2021).

Succinic Acid This is a versatile chemical that can be used in the production of bioplastics, resins, coatings, and more. It can be produced from lignocellulosic biomass through fermentation.

Lactic Acid This is another versatile chemical that can be used to produce biodegradable plastics, textiles, and more. It can be produced from agricultural waste like corn stover and wheat straw through fermentation.

Levulinic Acid This chemical can be used as a platform chemical for the production of a variety of products, such as solvents, fuels, and polymers. It can be produced from lignocellulosic biomass through acid hydrolysis.

Furfural This chemical can be used as a solvent, preservative, and building block for other chemicals. It can be produced from agricultural waste like corncobs, bagasse, and oat hulls through acid hydrolysis.

Cellulose Acetate This is a polymer that is used in textiles, films, and other applications. It can be produced from agricultural waste like cotton and wood pulp through chemical treatment.

These are just a few examples of the fine chemicals that can be produced from agricultural waste. With advances in technology and research, many other chemicals are also being explored for production from agri-waste.

16.2 Chemical Composition of Agricultural Waste

Agricultural waste, often known as agri-waste, comprises animal waste (animal carcasses and manure), waste of food processes as well as crop waste (sugarcane bagasse, corn stalks, drops and culls from vegetables and fruits), and agricultural toxic and hazardous waste (pesticides, herbicides, and insecticides) (Obi et al. 2016). These wastes typically are in the form of solids, liquids, or slurries. They are composed of various chemical components and compounds depending on the nature of the agro mass, growth conditions, system, and agricultural operations (Praspaliauskas et al. 2019). For instance, the type of livestock, stage of growth, and feeding practices, along with the quantity of bedding or water added to the manure, the type of manure storage, the length of time the manure is stored, and the weather circumstances, are the focal reasons that affect the nutrient composition of manure (Properties of Manure 2015). This biomass comprises 75% carbohydrates and 20% lignin, and the remaining consist of proteins, terpenes, oils, and fats (Alcántara et al. 2020). Generally, most agricultural waste constituents are cellulose, hemicellulose, and lignin. The chemical composition of various agricultural waste (wt% on a dry basis) is illustrated in Table 16.1.

16.2.1 Cellulose

Cellulose has been considered as a plant's cell wall and is the most prevalent naturally occurring linear carbohydrate polymer that contains D-glucose, representing approximately 40–50% by weight of the plant, and it is woody biomass. The chemical formula of cellulose is $C_6H_{10}O_5$ (Awogbemi and Kallon 2022). Due to its high strength, renewable nature, and ability for biodegradation, it is frequently employed in the production of paper, optical films, coatings, and textile companies.

Table 16.1 Chemical masterpiece of various agricultural wastes (wt% in dry basis)

Different waste materials	Lignin	Cellulose	Hemicellulose	Reference
Sugarcane bagasse	13.4	30.2	56.7	Shamsul et al. (2017)
Banana steams	5.2	33.3	18.2	Awogbemi and Kallon (2022)
Wheat straw	15	30	50	Lee et al. (2014)
Rice straw	19.5	38.8	27.6	Sadh et al. (2018)
Corn cobs	23	30	37	Briones et al. (2012)
Corn husk	4.1	47	43.9	Mohite et al. (2022)
Sorghum straw	10.3	35.4	19.4	Sadh et al. (2018)
Almond shell	27	39.3	28.8	Agricultural Waste Conversion to Activated Carbon by Chemical Activation with Phosphoric Acid (2007)

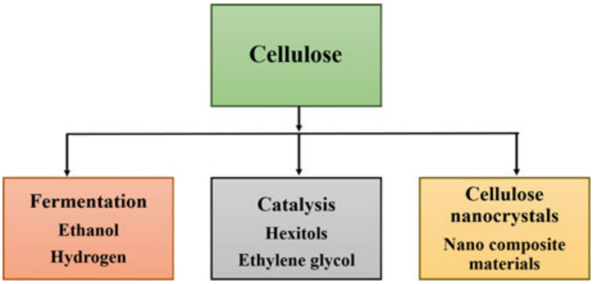


Fig. 16.1 Schematic representation of the application of cellulose (Kokel 2018)

It is common practice to extort cellulose from waste biomasses using mechanical, chemical, enzymatic, biological, and combinations of those treatments (Zhou and Wang 2020). Anaerobic bacteria ferment cellulose to produce ethanol, organic acids, and hydrogen. Furthermore, cellulose can be produced by biosynthesis. In an aqueous-culture media, bacterial cellulose is produced by microorganisms that consume hydrogen, nitrogen, carbon, and oxygen as food sources. Metal-catalyzed chemical conversion of cellulose produces a variety of chemicals, including hexitols and ethylene glycol (Kokel 2018), as depicted in Fig. 16.1.

16.2.2 Hemicellulose

Hemicellulose ($C_5H_4O_8$), which enfolds the cellulose fibers and links lignin and cellulose, is an amorphous, branched, heterogeneous polymer containing pentoses (arabinose and xylose), hexoses (glucose, galactose, and mannose), and acetylated sugars (Gundupalli et al. 2022). It is composed of a varied assemblage of branched polysaccharides. It has lower chemical resistance and is quickly hydrolyzed by weak bases, acids, and enzymes. Hemicellulose is used to produce industrial chemicals and other high-value products, despite having less physical strength, crystalline structure, and low molecular weight than cellulose (Awogbemi and Kallon 2022). This polysaccharide polymerization is near the ground without a crystalline constituency. As a result, it can be rapidly degraded into monomers (Sathendra et al. 2022).

16.2.3 Lignin

Lignin is a noncarbohydrate multifarious aromatic polymer by nature. It succeeds itself by the polyphenolic arrangement as a possible biobased renewable and sustainable feedstock for the manufacture of aromatic fine chemicals (Zirbes and Waldvogel 2018). It is attached to cellulose and hemicellulose and assists in providing the material's cell wall strength and solidity. Further, it produces an invisible barrier that is immune to microbial attack and resistant to aqueous, physical, and chemical attacks. The general molecular formula of lignin is $C_9H_{10}O_3(OCH_3)$, and it consists of syringyl, *p*-hydroxy phenol, guaiacyl, and other macromolecules. The components and composition of lignin vary in different plants (Zhou and Wang 2020). Constructive energy stability of biorefinery concepts requires the utilization of lignin into suitable value-added compounds, such as fine chemicals or fuel additives (Lölsberg et al. 2015). Hence, major attention has been waged on the lignin extraction process from plant-based waste biomass. It can be used as an absorbent, antioxidant, dispersant, binder, and so on, which predominantly anticipates its arrangement with hydrophobic elements (Zhou and Wang 2020). Various efforts have been made to effectively degrade the biopolymer into appropriate compounds (Zirbes and Waldvogel 2018). Even though lignin has been transformed into value-added compounds by numerous technical domains, industrially useful lignin depolymerization into products is still in its infancy. Electrochemical cleavage of lignin is one of the industrially shown potential valorization technologies (Manuscript 2016). Attributable to its complicated structure, the valorization of lignin is the most challenging process in biorefining, being the only enormous capacity renewable feedstock that is calm of aromatics (Volf and Popa 2018).

16.2.4 Collagen

Collagen is the most abundant component of collagenous waste solids (e.g., skin, tendons, and muscle) produced by the fishing processes, poultry, leather trimming, and other industries. It is a fibrous, biodegradable, and biocompatible protein found in animals that accounts for approximately 30% of the total protein in the body. Numerous familiar methods exist to segregate collagen, including neutral saline solutions, acid solutions, and acid solutions with enzymes (Zhou and Wang 2020).

16.2.5 Keratin

Keratin is the most important component, which is present in chicken or bird feathers, hair, bristles, hooves, horns, and nails. Million tons of keratin richer wastes are produced every annum over the planet, classically in the poultry slaughter process and the fabric textile industry; soluble keratin is obtained by thermal treatment, hydrolysis (e.g., acid, alkaline, and enzyme), steam flash explosion, and oxidation or reduction of disulfide bonds (Zhou and Wang 2020).

16.3 Fine Chemicals and Their Potential Uses

Fine chemicals are the chemical stuff contrived with an extreme degree of purity for a specific purpose. They have been produced in tiny and restricted quantities in plant life using batch or biotechnological processes. Fine chemicals are technology-intensive, commercially strong, high value-added chemical products (Hara et al. 2014).

In modern existence, the production of large ratios of fine chemicals in the chemical industry has progressively amplified (Xu 2021). Petroleum-based originators facilitated the production of fine chemicals while also causing the unintentional release of toxic waste. As a result, agricultural wastes and by-products have been used to generate value-added products such as fine chemicals, biopolymers, biomaterials, biofertilizers, bioplastics, organic acids, single-cell protein (microbial biomass), and enzymes. These precious biomaterials are widely used in the chemical, cosmetics, beverage, pharmaceutical, and food industries (Capanoglu et al. 2022). For instance, 5-hydroxymethylfurfural (5-HMF) is a highly precious biomass-derived complex produced by the dehydration of carbohydrates (glucose, fructose, cellulose, and sucrose), which is habitually used for the production of pharmaceuticals, plastic, liquid fuels, and fine chemicals. A diverse variety of active ingredients and sophisticated intermediates are included in fine chemical synthesis. The distinctions between specialty, commodity, and fine chemicals are listed in Table 16.2.

Commodity chemicals are the mass production by continuous process in chemical industries to satisfy worldwide demand. On the other hand, specialty chemicals are the combinations of two or more fine chemicals that result in a mixture for a particular purpose. Specialty chemicals are occasionally referred to as effect or performance chemicals because the focal point is their accomplishment in the end user's function (Mohite et al. 2022), as presented in Fig. 16.2.

16.3.1 Potential Uses of Fine Chemicals

Biopolymers are other most imperative products acquired from food wastes and by-products, comprising a broad range of products. However, these biopolymers are worn in significant applications in various industries like cosmetics, medicine, food,

Table 16.2 The difference between commodity, specialty, and fine chemicals

Commodities	Specialty chemicals	Fine chemicals
Single basic chemicals	Mixtures of fine chemicals	Single complex chemicals of ultrahigh purity
High volume production Low cost	Quantities and costs based on end-user industry	Low volume production (<1000 tons year^{-1}). High cost ($>\$10$ kg^{-1})
Mass production by the continuous process, using consistent reactions to meet global demand	Blended with customized batches	Production with customized batches
Exploit is based on their flexibility as raw materials	Exploit is based on explicit functionality	Exploit is based on explicit molecular personality

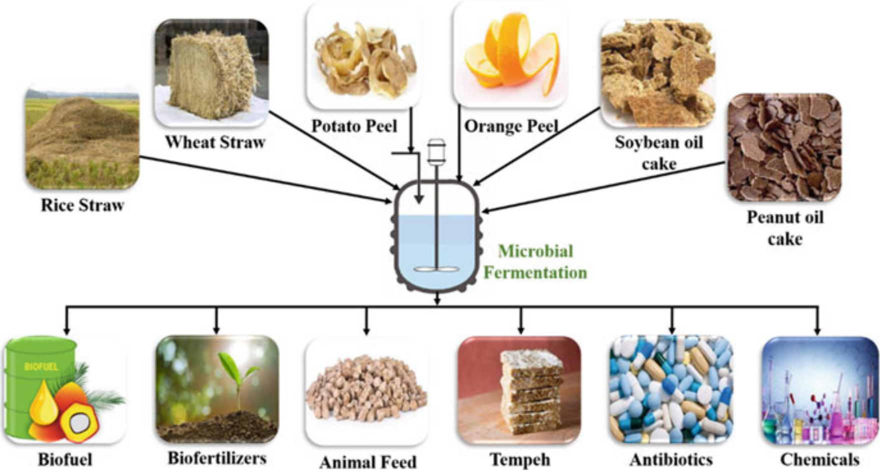


Fig. 16.2 Application of agricultural waste (Sadh et al. 2018)

pharmaceutical, water treatment, biosensor, plastic, and clothing and fabric industries because of their bio-functionality, biodegradability, bio-stability, and biocompatibility.

16.3.1.1 Pharmaceutical Drugs

Globally, the pharmaceutical industry represents nearly two-thirds of the demand for fine chemicals, making it the most significant customer by far. Different antibiotics are produced using various agricultural wastes (Sadh et al. 2018). One reason fine chemicals are most important is the position they play in the production of pharmaceutical drugs. Hydrogen, for example, is a fundamental chemical repeatedly used in pharmaceuticals. Phenolics can also be extracted from potato peel which is a significant antioxidant. Moreover, Rice bran-based phenolic compounds like caffeic acid, ferulic acid, and ferulate can potentially prevent various chronic diseases like human breast and colon cancer (Amran et al. 2021). Peptide production from natural resources, including agri-wastes, has diverse applications, such as being antimicrobial, for tissue regeneration, as cancer drugs, and for drug delivery attributable to their tunable functionalities and biocompatibility (Kokel 2018).

16.3.1.2 Food Application

Acid chlorides, for example, are useful in the food service industry since people can utilize them as preservatives in animal and human food products. Propanoic acid, a clear liquid with an unpleasant odor, is an example of an acid chloride used as preservative. Acid chlorides also were found in food product lines such as vinegar. Ethanoic acid is an essential constituent of vinegar and represents the liquid form of acid chlorides. Butanoic acids can be encountered in dairy products like milk and butter. Numerous food products, such as butter and vinegar, comprise fine chemicals in their ingredients. Agrochemicals are also employed to protect crops against pests and boost crop yields (Sathendra et al. 2022).

16.3.1.3 Agricultural and Fertilizer Application

Biofertilizers are formed from readily accessible organic matter such as vegetable wastes, molasses, bamboo, rice husk, and so on, which can be identified mostly in remote areas. Biobased fertilizers are environmentally sustainable alternatives to dangerous chemical fertilizers. People convert organic compounds into fertilizers that can be utilized to keep crops productive and healthy. Using these organic compounds can minimize the cost of production due to them being made from readily accessible organic material (Pratik and Surekha 2018).

Using animal wastes as fertilizer seems to have a massive effect on agricultural inputs' energy needs. Through inorganic fertilizers, compost might deliver 38%, 19%, and 61% of the phosphorus, nitrogen, and potassium, respectively. Fertilizer use of massive confinement manures, on the other hand, is linked to high energy costs for mobility, dispersion, giant warehouse requirements, odor issues, and the probability of groundwater pollution. Rice straw composting, together with animal dung, could be used to enhance soil fertility and control soilborne illnesses. In order to generate a high nutritional fertilizer, rice straw was combined with animal manure or municipal raw sewage and composted quickly. This compost was used in fungicide management strategies to minimize the use of synthetic fungicides and leachate disposal. Rice husk is composed of two polyphenolic compounds, silica and lignin, and it contains 67% of volatile matter, 15% of carbon, and 18% of ash. Because of the silica and lignin content, the husk has antioxidative and antibacterial properties. The elevated lignin substance is also used for soil amendments, while silicon and potassium are used to amend soil (Amran et al. 2021). Agrochemicals are also employed to improve agricultural gains by safeguarding crops from insects and ramping up crop productivity. Fine chemicals, for example, are utilized in pesticides, making them vital to agriculture.

16.3.1.4 Alkaloids

Alkaloids seem to be nitrogen-containing artifacts from amino acids found in plants, such as lysine, histidine, tryptophan, ornithine, and tyrosine. The majority of them are used for the medicinal and biological application fields. They are primarily derived from natural sources for practical needs, but productivity is very low due to plants producing low alkaloids concentrations (Hara 2014). Toxins accumulate in agricultural residues due to the use of pesticides, insecticides, herbicides, and other chemicals in crop production. Steroidal alkaloids are abundant in potatoes. Pollutants from agricultural insight must be characterized and separated before they can be converted into valuation products that are secure for both the environment and humans. Steroidal alkaloids are potentially toxic metabolites with antifungal, antibacterial, and insect-repellent characteristics. These substances have been linked to diarrhea, colic pain, gastroenteritis, fever, vomiting, and low blood pressure (Amran et al. 2021).

16.4 Synthesis Routes of Fine Chemicals from Agricultural Waste

Fine chemicals can be synthesized by utilizing agricultural wastes, typically from carbohydrates, proteins, and lipids, through three main routes: physical refining, chemical, and biochemical routes. Polysaccharides such as cellulose, starch, and lignin (to synthesize aromatic compounds) are a hopeful source for developing biobased fine chemicals. Agricultural wastes, including crop residues (i.e., corn stover and sugarcane bagasse), forest waste, sawdust, and leaf litter, are typical lignocellulosic biomass resources. The production is a multifaceted batch or semi-batch process that produces an ultrapure chemical with compulsory specifications (Hodaifa et al. 2019). Since fine chemicals are thermally unstable, they are produced in the liquid phase at moderate temperatures.

Biochemical Conversion Agricultural waste can be converted into fine chemicals using enzymes or microorganisms that break down the waste into smaller molecules. For example, lignocellulosic biomass can be hydrolyzed into simple sugars, which can then be fermented into biofuels or other chemicals like succinic acid or lactic acid.

Thermochemical Conversion Agricultural waste can also be converted into fine chemicals using high temperature and pressure in the absence of oxygen. This process is called pyrolysis or gasification and can produce products like bio-oil, syngas, and biochar.

Chemical Conversion Agricultural waste can be chemically treated to convert it into fine chemicals. For example, cellulose can be chemically treated to produce cellulose acetate, which is used in textiles and films.

Overall, the conversion of agricultural waste into fine chemicals can be a sustainable way to valorize waste and reduce the reliance on fossil fuels.

16.4.1 Physical Refining

Physical refining process is the simplest and most cost-effective route of fine chemical synthesis from carbohydrate and lipid-containing biomass feedstocks. This production category includes distillation, extraction, and thermolysis (e.g., pyrolysis, liquefaction, and gasification) processes. In the thermolysis process, biomass resources are primarily converted either to synthesis gas or a mixture of small molecules and bio-oils (e.g., carboxylic acids) and further to intermediates and end products by classical synthesis routes.

16.4.2 Chemical Synthesis

Chemical schemes for producing fine chemicals include the use of potentially dangerous substances such as sodium borohydride, as well as ridiculously priced metals and complicated precursor active ingredients (Finnigan et al. n.d.). Chemical synthesis intended for fine chemical production is highly energy intensive and environmentally non-suitable since it passes through different stages: (1) degradation of functionals found in biomass to C_1 molecules or hydrocarbons and (2) hydrocarbons and methanol to intermediates and finally to end products to re-functionalize.

16.4.3 Biochemical Process

Fungi and bacteria are the two types of microorganisms that deteriorate lignocellulosic biomass. The former plays a significant role in wood degradation. White and brown rot fungi represent the most widespread and efficient hemicellulosic and lignin-deteriorating microorganisms (Kokel 2018). Microorganisms that excrete ligninolytic enzymes fractionate the lignin content in biomass, disrupting the native structure, and then hydrolyze holocellulose with enzymes to emancipate monomers. Fine chemicals like nutritional supplements, pharmaceuticals, cosmetics, flavoring agents, and additives of foods and fertilizers are formed through microbial or enzymatic fermentation (Hara 2014). The biochemical production route occurs at lower temperatures relative to chemical and physical approaches. Biochemical productions are generally a green alternative, and the processes are not hazardous to the environment (Tramontina et al. 2020). However, the enzymes are limited and expensive and discharge waste during the purification of the target product. Host enzymes are primarily *Escherichia coli* and other microorganisms such as *Bacillus strains*, *Saccharomyces cerevisiae*, *Corynebacterium glutamicum*, *Aspergillus* *oryzae*, and *Streptomyces* strains that are used in fermentations to synthesize various fine chemicals based on their distinct metabolic pathways (Hara 2014).

16.5 Recent Improvements in Conversion Technologies

Besides feedstocks and other inputs, improved conversion technologies are currently crucial for environmentally affordable and economically feasible production of fine chemicals and waste management. Various technologies are selected and improved to direct the processing moment in time, the production progression of fine chemicals, and any process control related to information technologies (Cortez et al. 2021). Biomass residues such as agricultural wastes have gained global attention as promising renewable and sustainable resources for inventing cost-effective fine chemicals (biobased chemicals). Synthesis of fine chemicals involves different conversion technologies: chemical synthesis, extraction, hydrolysis, and recently improved technologies such as electrosynthesis (Zirbes and Waldvogel 2018) and biotechnology (Tramontina et al. 2020). Among these technologies, chemical and biotechnology ways of synthesis are the chiefly frequently utilized approaches, occasionally used by a combination of both (Rinaldi et al. 2016). Different literatures are also reported on the production of fine chemicals (e.g., aromatic fine chemicals) from lignin using thermolysis, hydrolysis, and homogeneous and heterogeneous catalysis conversion methods (Rinaldi et al. 2016; Xu et al. 2014). Fine chemical production can be done in multipurpose plants. Availability of the production equipment is high, and installation of the equipment is also simple. So, employing these technologies is easy and saves overall time. Using an improved conversion technology for fine chemical production generally helps to achieve higher efficiency and saves costs by managing waste disposal.

16.5.1 Chemical Synthesis

Chemical synthesis methods are effective tools for processing biomass-based fine chemicals. Chemically, the invention of fine chemicals can be performed from petroleum-based starting chemicals such as propylene, ethylene, and benzene or extracts of natural products. Several fine chemicals are found in natural product extracts in which these extracts have typically existed in plants. Chemical conversion can be performed through catalytic or non-catalytic processes. Catalytic conversion of agricultural wastes to biobased fine chemicals and polymer processes further involves heterogeneous or homogeneous catalysts. Heterogeneous catalysis conversion processes are effective and environmentally safe approaches due to less waste removal in the product purification stage and also catalysts and can be reused for the same target. Fine chemical synthesis from carbohydrate biomass is a sustainable technology that reduces greenhouse gas emissions and avoids the instabilities of expenditure and accessibility of fossil fuel-based resources (Rinaldi et al. 2016).

16.5.2 Biotechnology

Biotechnology, particularly fermentation, is the most well-known and influential technique in producing high-quality fine chemicals. It has been employed to spiritualize agricultural residues and by-products by transitioning them into functional components (Capanoglu et al. 2022). It also is an enhanced conversion system for the invention of biobased high-quality fine chemicals. This system involves the utilization of renewable biomasses such as carbohydrates and vegetable oils and an effective renovation of conservative feedstocks into fine chemicals (e.g., polyphenols and 6-aminopenicillanic acid), specialties (e.g., food and fertilizer additives), and commodities (e.g., succinic acid). Biocatalysis, cell cultures, and bio-formation (microbial fermentation) are the three areas of bioconversion technology for fine chemical production. Biocatalysis involves enzymes performing a chemical transformation for enhancing the production of organic compounds. Biocatalysis is faster and minimally energy demanding and produces very little waste throughout the biosynthetic pathways of fine chemicals. As a result, it is simultaneously environmentally friendly and cost-effective. The biosynthetic pathway, the alteration of natural matter into fine chemicals through microorganisms, is employed to produce small molecules (via enzymes in whole cell circuits) as well as less complicated non-glycosylated big molecules such as peptides and relatively simple proteins. For 10,000 years, the technique has been utilized to develop food products such as alcoholic beverages, yogurt, cheese, and vinegar. A biosynthetic process, unlike biocatalysis, does not rely on chemicals as precursor materials but rather on inexpensive natural biomass resources such as glucose to represent a nutrient for the cells. Biosynthetic pathway is a complicated process that converts simple substrates into more advanced components. Plant cell culture eliminates cells from tissues and continues to develop if farmed under the right nutrients and constraints. Cell culture refers to the process of growing cells outside of their natural habitat (Hara 2014).

16.5.3 Synthetic Bioengineering

Artificial bioengineering is a novel approach that was previously developed to construct optimized microbial cell production of plants to effectively produce active compounds via fermentation. Artificial bioengineering uses molecular genetic perspectives to orchestrate metabolic pathways to improve the biosynthetic possibilities of well-characterized broadcast strains. This converting technique is accomplished through the use of genetic engineering approaches based on artificial metabolic layouts created through computer modeling. The quantities of substrates and enzymes in enzymatic reaction blends are easily controlled; regrettably, this is challenging in fermentations, even though precursors could be shuffled through various metabolic pathways (Hara 2014).

Production of biobased fine chemicals through microbial fermentation instead of enzymatic reactions reduces costs due to using less expensive substrates. To advance the creation of fine chemicals over microbial fermentation systems, the genes coding the required enzymes are introduced into a fitting host strain. Since it has a well-developed genetically engineered mechanism and capacity to express elevated levels of genes that encode desired enzymes, *Escherichia coli* is frequently chosen as the primary participant for developing desired enzymes. Microorganisms such as *Bacillus* strains, *Corynebacterium glutamicum*, *Saccharomyces cerevisiae*, *Aspergillus oryzae*, and *Streptomyces* strains, on the other hand, are chosen as fermentation hosts based on the unique metabolic pathways needed to produce target products. Fine chemicals such as aromatics, γ-aminobutyric acid, peptides, isoprenoids, oligosaccharides, and polyphenols are some of the newly urbanized and additionally well-categorized biobased chemicals produced through synthetic bioengineering conversion approach.

16.5.4 Extraction

Rather than synthesizing natural biopolymers, biobased molecules, and phytochemicals from petro-based chemicals, they can be directly obtained through extraction. Once extracted, these beneficial biobased products are known as greater products like nutraceuticals, food additives, therapeutics, cosmetics, and nutraceuticals (Hara et al. 2014). Extraction of various products from plants or animals could be permitted during the development of fine chemicals. Fine chemicals are extracted through liquid-liquid solvent extraction; the solvents are diethyl ether, ethyl acetate, and chloroform or solid-phase extraction, conditional on the solubility of the desired product. Extraction can be affected by factors such as the characteristic and particle size of the feedstock, desired fine chemical structure, extractive separation process techniques, the involved solvent, and the presence of interfering compounds. Finally, during isolation and purification of the desired product, fine chemical will occur after the extraction time elapsed due to pressure, temperature, and density differences. Microwave-assisted (Calinescu et al. 2017), ultrasound-assisted, and supercritical fluid extraction (Šavikin et al. 2017) processes are the most improved and selected economically and environmentally safe conversion technologies applied to separate various biobased fine chemicals. Structure blocks for peptide synthesis, amino acids, are isolated from a protein containing plant agricultural residues through physical, chemical, or biochemical processes. Because amino acids are hydrophilic, physical separation necessitates the utilization of a macromolecule that produces a steady hydrophobic compound with amino acid by hydrogen bonding protonated amide group.

Essential Oils These are concentrated liquids that contain aromatic compounds from plants. Essential oils can be extracted from agricultural waste like citrus peels, herbs, and flowers using steam distillation or cold pressing.

Pigments Agricultural waste like fruits and vegetables can be a source of natural pigments that can be extracted and used as food colorants or in other applications. Examples include anthocyanins from grape skins and betalains from beetroot.

Tannins These are plant polyphenols that can be extracted from agricultural waste like grape pomace and tea leaves. Tannins have applications in tanning leather, making ink, and as a natural preservative.

Flavonoids These are plant compounds that have antioxidant and anti-inflammatory properties. Flavonoids can be extracted from agricultural waste like citrus peels, grape skins, and soybean hulls.

Proteins Agricultural waste like soybean meal and peanut shells can be a source of protein that can be extracted and used in animal feed or as a nutritional supplement.

Enzymes Agricultural waste like pineapple stems and apple pomace can be a source of enzymes that can be extracted and used in various industrial processes.

Polysaccharides Agricultural waste like wheat bran and corn cobs can be a source of polysaccharides that can be extracted and used in food, pharmaceuticals, and cosmetics.

These are just a few examples of the extractive products that can be obtained from agricultural waste. Different methods like solvent extraction, supercritical fluid extraction, and enzymatic hydrolysis can be used to extract these products from the waste.

16.5.5 Hydrolysis

Hydrolysis degrades polymers (proteins, carbohydrates, and lipids) into monomers and dimers using hydrolytic enzymes excreted by acidogenic microbes (Pratik and Surekha 2018). Hydrolysis of agricultural waste proteins can occur when making fine chemicals, where proteins are subdivided into amino acids. It is a relatively simple procedure that entails heating the protein in the presence of an ion exchange chromatography active catalyst for an extended time period. The reaction segregates the amino acids, which are then used to make fine chemicals. Cellulose hydrolysis with recently selected solid catalysts (such as Lewis acid reagent catalyst, encrusted transition oxygenated metal acidic resins, acid-personalized amorphous carbon, and zeolites) primarily yields reducing sugars and further conversion to various fine chemicals using a multistep fractionation process (Guisnet et al. 2006). Protein hydrolysates, antioxidants, oligosaccharides, pigments, and innovation substrates are among the many products produced from food waste using these enzyme complexes (Capanoglu et al. 2022).

16.5.6 Biorefining Conversion Technologies

The biorefining process involves a well-organized fractionation of biobased feedstocks into different fine chemicals, energy, and bio-crude for fuel using physical segregation methods with the combination of thermochemical and biochemical alteration routes. The biorefinery conversion technique takes place through three main stages:

1. Segregation of biobased feedstock into their individuals (proteins, cellulose, lignin, hemicelluloses, amino acids, minerals, pure plant oil, pharmaceutical compounds, and fine chemicals) through filtration, solvent extraction, and distillation processes.
2. Alteration of midway fractions to precious final products (e.g., biofuels and intermediates for fine chemicals like as acids or alcohol and platform chemicals of phenolic compounds or lactic acid). The second alteration stage is possibly performed through thermochemical conversion techniques (e.g., gasification, pyrolysis, and liquefaction) and biochemical techniques (e.g., fermentation).
3. Finally, chemical intermediates are processed to high value-added end products (Volf and Popa 2018).

Biorefining conversion technologies are environmentally and economically sustainable to minimize energy utilization, waste accumulation, and the value of end products with zero waste. The biorefining schematic process is represented in Fig. 16.3 for cellulosic biomass into fine chemicals.

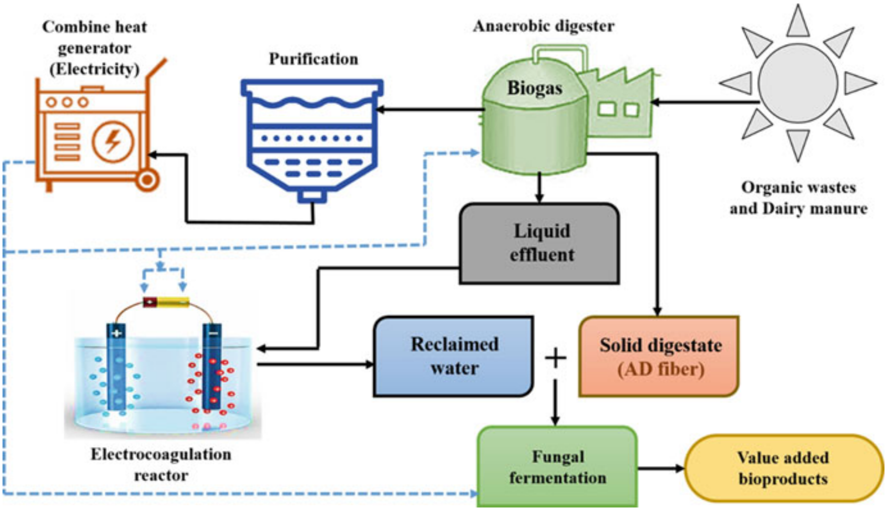


Fig. 16.3 Biorefining technology of cellulosic feedstocks for fine chemical production (Liu et al. 2016)

16.5.7 Electro-Conversion Synthesis

Electrosynthesis is one of the recently improved green suitable conversion technologies for the invention of biobased bright chemicals. Electrosynthesis of organics is the artificial technique that allows the utilization of electrical power for the invention of precious compounds (Waldvogel et al. n.d.; Yan et al. 2018). In this conversion method, chemical oxidizers or reducing agents are directly substituted by electrical energy as reagents; thus, redox reaction will take place. Electrosynthesis is a sustainable, prevailing, and green technology for consuming renewable agricultural waste such as stream lignin (Nguyen et al. 2015; Zirbes and Waldvogel 2018). Recently selected and improved conversion technologies for producing different fine chemicals are indicated in Table 16.3.

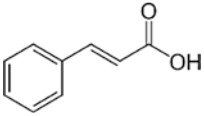
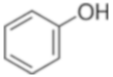
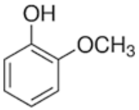
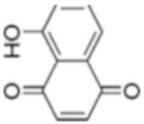
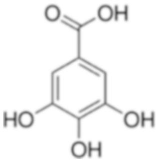
16.6 Commercialization Opportunities

The market of fine chemicals is spread internationally. Most of the products used for people's daily intake contain ingredients that have fine chemicals. Medication someone took, processed foods, insecticides, and agrochemicals such as herbicides and fertilizers are made of fine chemicals. Fine chemicals are pure substances synthesized for multiple purposes in different plants (e.g., as preparatory supplies for specialty chemicals). This is achieved through formulation directly or through intermediate transformation through chemical/biochemical schemes to end products. The electrical industry and the automotive industry predominantly drive the fine chemical market. The rapid expansion of end-user industries increases the demand and utilization of fine chemicals; thus, the market opportunity is rising daily. The predominantly pharmaceutical sector, followed by food industries and agrochemicals, is the principal customer for fine chemicals. Electronics, automotive, cosmetics, and construction sectors are also contingent on fine chemicals.

Fine chemical-producing industries are mostly situated between the customers (e.g., agrochemical and specialty chemical industries), products, and suppliers. Different fine chemicals are sold for their perspective applications:

1. Plant health products such as herbicides and pesticides destroy and mitigate any herbs and pests. These products are manufactured through a chemical synthesis approach.
2. Fragrance and flavor additives are commercialized for producing perfumes and flavoring foods and beverages.
3. Active pharmaceutical ingredients have been synthesized and modified for medicinal products and drug production.
4. Many peptides can be commercialized to be used as antimicrobial agents. For example, an original peptide is presently being studied in clinical assessment to treat fungal or bacterial infections, focusing on cutaneous and catheter-related infections (Zirbes and Waldvogel 2018).

Table 16.3 Recently selected and improved conversion technologies for the production of different fine chemicals

Conversion technology	Synthesis method	Feedstock	Fine chemical category	Structure of the fine chemical	References
Electro-conversion		Lignin	Aromatic fine chemicals		Zirbes and Waldvogel (2018) and Manuscript (2016)
Biorefining	Chemical and biochemical	Biomass resources	Polyphenols		Volf and Popa (2018)
Biotechnology (biocatalytic)	Biochemical	Waste plant biomass	Aromatic fine alcohol (coniferyl)		Tramontina et al. (2020)
Microwave-assisted extraction	Physical refining	Sea buckthorn leaves	Quinones		Calinescu et al. (2017)
Ultrasound-assisted extraction	Physical refining	*Thymus serpyllum* L. herb	Polyphenols		Šavikin et al. (2017)

5. Fine chemicals were utilized to create specialty chemicals with specific properties required for their intended end use.

16.7 Conclusion

Agricultural wastes can be considered as feed material for fine chemicals, biofuels, biofertilizers, food and pharmaceutical industries, or traditionally animal feed. Various agricultural wastes are utilized to produce fine chemicals through physical, chemical, and biochemical production routes. Currently, organic fine chemicals are synthesized through enhanced and advanced production methods such as microwave-assisted extraction and biochemical methods and biosynthetic and electrolysis conversion technologies. Predominantly lignocellulosic agricultural wastes and carbohydrates and extractives such as lipids are the possible feedstocks for economically affordable production of fine organic chemicals. Further, the production is interesting for reducing environmental problems regarding waste discarding and social benefits and rural development of one's country. The distribution of fine chemicals is wide-reaching, and the products have high commercialization opportunities since they are cast off directly or as raw material for specialty chemical industries. Thus, a production based on market-led novelty and developing technology supports a new growing market.

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Centralized Approach for the Agricultural Waste-Based Industry

17

Krishna Das, Aishi Nath, and Ganesh Chandra Dhal

Abstract

Urbanization, changes in lifestyle, and population growth have caused uncontrolled agricultural waste production, including animal agriculture, crop production, animal production, and pesticide use, leading to environmental damage if not managed properly. Animal production contributes to 66% of NO_x and 37% of methane, while burning agricultural waste in incinerators worsens climate change and decreases agricultural output. Solutions for sustainable agricultural waste management have adverse effects, and two approaches are available: centralized and decentralized treatments. Decentralization is increasingly becoming the preferred approach due to new technology, engineering, and financial structures. Recovering and reusing agricultural waste are necessary due to population growth and climate change, but centralized systems may not be the best option economically and environmentally. This chapter examines the optimal degree of centralized waste collection and treatment and the advantages and disadvantages of various techniques over time.

Keywords

Agricultural waste · Sustainable alternatives · Centralized · Decentralized

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17.1 Background

To meet the needs of a rapidly expanding global population, agricultural wastes (AWs) are produced daily in huge quantities. Because these resources are not being managed well, there is an urgent need to find ways to use them at the right time to ensure that agriculture is sustainable and that people have food and health security. Waste from farming has been around since people started growing crops more than 10,000 years ago. At the same time, people began cultivating crops, and AW was not simply burned or abandoned. It was repurposed. In Scotland, archaeologists have discovered AW to be approximately 12,000 years old and utilized as compost to improve agricultural outcomes. Historical records show that AW was frequently recycled in Mesopotamia, Greece, Rome, and China. Strawboard was created from AW in the Netherlands. Between 1870 and 1970, leftover straw was used to produce cardboard in the northern Netherlands and neighboring German regions. The sources of AWs include crop residue, agro-industries, livestock, and aquaculture. The environmental impact of AWs and their treatment make them a global issue. AWs can contribute to air and water pollution and global warming without adequate management. Burning AWs is a typical method of disposal, which releases air pollutants like particulate matter, carbon monoxide, and greenhouse gases (GHGs). In addition to contributing to climate change, this can have severe health consequences for those living near the burning areas. AWs are also disposed of by burying them in landfills, which can lead to the contamination of groundwater and the generation of methane gas, which is another harmful GHG. Certain crop wastes have historically been used for various reasons, including burning, animal feed, roof thatching, composting, soil mulching, match-making, and paper production. These measures can aid in minimizing the environmental impact of AWs and bring economic benefits to farmers and communities.

Therefore, it is essential to discover sustainable ways to manage AWs, such as utilizing them for energy production or as feedstock for bioproducts, to decrease their harmful effects on the ecosystem and climate (Koul et al. 2022). Improper disposal of AW might result in various negative side effects. When AW is improperly disposed of, hazardous gases such as N_2O, SO_4, and CH_4 are released, which can contribute to global warming and climate change. In addition, the combustion of AW can emit smoke and particle matter, which can cause significant air pollution and threaten human health. Inappropriate disposal of AW can also contribute to regional environmental damage, especially regarding soil and water quality. When pesticide waste is incorrectly disposed of, for instance, it can contaminate soil and water resources, causing harm to ecosystems and posing a risk to human health. In addition to the environmental damage that improper disposal of AW might cause, it is also vital to consider potential economic losses. When crop straws are burned in open air, for instance, the chance to utilize that material for more profitable uses, such as composting or energy production, is lost. Therefore, it is crucial to establish waste management (WM) systems for AW that minimize environmental damage and maximize economic benefits. These may include composting, biogas production, and enhanced waste segregation and collection systems. Both the environment and human health can be preserved by tackling the issue of AW disposal (He et al. 2019).

During AW collection and treatment planning, the degree of infrastructure centralization is one of the most important factors that must be considered. The selection of the most effective method for the management of AWs is not a simple process as it requires the evaluation of numerous factors that are typically difficult to assess. It is recognized that both centralized and decentralized managements are valid approaches in general. In decentralized systems, waste is treated close to its source. Contrarily, in centralized systems, waste is collected and treated at a waste treatment plant (WTP) outside the region being serviced. Before the middle of the nineteenth century, decentralized WM was the most prevalent practice. As a result of rising urbanization and the need for economies of scale, there is a desire for centralized WM, particularly in rural and hilly regions. Energy recovery from biodegradable organic matter is possible if anaerobic digestion is adopted for waste stabilization and biogas production; however, this choice requires careful consideration because its success is subject to economies of scale and is highly dependent on the characteristics of waste; this creates additional issues regarding the selection of the appropriate degree of centralization (Pasciucco et al. 2022).

Appropriate WM is essential for sustainable development in various urban contexts and socioeconomic realities across the globe, including in developing nations, metropolitan centers, and places without unique water challenges. Proper WM can aid in reducing pollution, promoting public health, and conserving resources. A central authority, such as a government agency or private corporation, collects, transports, and disposes of waste as part of centralized WM. This strategy can be useful in densely populated places with limited waste disposal space, but it can be expensive and unsuitable for many communities. Local communities manage their waste through activities such as composting, recycling, and waste reduction under decentralized WM. This strategy has the potential to be more sustainable and cost-effective, but it may necessitate greater community involvement and education. Several authors have analyzed the advantages, disadvantages, and differentiating features of centralized and decentralized WM strategies. In certain instances, the most successful option for a given community or region may be a hybrid strategy that includes both components. Due to their great populations and high consumption levels, the USA and China face significant WM difficulties. Both nations have devised various WM systems to solve these difficulties, including centralized and decentralized alternatives. WM must be customized to the demands and reality of each community or region to contribute to sustainable development. However, Gikas and Tchobanoglous argue that decentralization can be applied at numerous scales, with WTP sizes ranging from small to large (Pasciucco et al. 2022). In many circumstances, decentralized systems are small facilities that serve no more than a few thousand population equivalents. Various intermediate solutions are available between the two extreme situations of complete centralization and onsite treatment. The only legitimate definitions of centralized or decentralized systems apply to the distance between the site where waste is produced and the treatment facility. Evaluating the best amount of centralization is not a straightforward process;

hence, planners and decision-makers must use decision support systems to aid them in determining the optimal solution.

This chapter presents an analysis of research investigating the degree to which waste collection and treatment systems are centralized, emphasizing the decision-making procedures utilized. It will analyze and compare various technical approaches, focusing on their distinct benefits and drawbacks and their development throughout. The major goal is to assist planners and decision-makers so that they may pick and apply the most appropriate approaches for measuring the degree to which waste facilities are centralized.

17.2 Agricultural Waste or Agro-Waste (AW)

In most nations, AW is misdirected or abandoned due to a lack of awareness or a sufficient conduit for its transmission and utilization. For economic growth, the majority of agriculture-dependent nations must prioritize the reuse of agricultural and agro-industrial waste. It increases the local farmers' economy and the national economy. Utilizing these wastes reduces imports of fossil fuels and other agricultural fertilizers. Utilizing AW has innumerable positive effects concerning pollution on air, water, and soil. Ending the era of fossil fuels must be accompanied by a successful transition to biofuels if nature is to be protected and climate change is to be contained (Khan et al. 2022).

AWs are nonproduct outputs of producing and processing agricultural products that may contain human-beneficial material but whose economic value is less than the cost of collection, transport, and processing. Estimates of AW are uncommon, although it is commonly believed to contribute a considerable fraction of the developed world's total waste. The wastes generated by the irrational use of intensive farming practices and the misuse of agricultural chemicals can substantially affect rural and global environments. Monoculture, excessive use of pesticides and fertilizers, and overgrazing are examples of intensive farming methods that can lead to soil degradation, biodiversity loss, and contamination of water sources. This can result in decreased productivity, crop yields, and negative consequences for agriculturally dependent local people.

Additionally, the waste generated by these methods might potentially contribute to climate change. For example, synthetic fertilizers and pesticides can contribute to higher emissions of GHGs. At the same time, the conversion of natural habitats for agriculture can result in the release of carbon held in the soil and vegetation. In addition to negatively affecting the environment, the waste produced by intensive farming operations can be hazardous to human health. Exposure to pesticides and other chemicals can result in acute and chronic health problems, including respiratory issues, skin irritation, and cancer. To overcome these difficulties, it is vital to encourage more sustainable agriculture methods that limit the use of chemicals, improve soil conservation, and safeguard biodiversity. This can include organic agriculture, agroforestry, and integrated pest management. Effective WM and disposal are also vital to limit the harmful effects of AW on the environment and human health. Overall, the waste generated by intensive farming practices and the misuse of agricultural chemicals significantly impact rural and global environments. It is vital to implement more sustainable behaviors and better WM solutions to offset these impacts and achieve a more sustainable future. AW is produced by various sources, the most common of which are farming, livestock farming, and aquaculture. These wastes are being put to several different uses, thanks to the method of WM known as "3R." AW risks the health of all living things, including humans, animals, and plants, through various direct and indirect paths.

Every year, agriculture produces around 700 million metric tons of waste (Hoang et al. 2023). AW comprises the discarded parts of plants used in agriculture. Agriculture and horticulture are the industries that are responsible for producing these waste streams. The term "agricultural waste" refers to any components of plants that are not used for food production for humans or animals. Most of this is made up of the plant's stems and leaves. It is claimed that AW makes up approximately 80% of the plant material in such crops on average (Nwakaire et al. 2016). Sugarcane, maize, cereals, and rice are the four types of agricultural products that are cultivated the most frequently. Considering that 80% of this is waste from farms, there are still billions of kilograms of waste from farms worldwide. Every year, agriculture produces around 700 million metric tons of waste (Hoang et al. 2023).

17.3 Composition of Agricultural Wastes

The Food and Agriculture Organization estimates that approximately 36% of the world's land is suitable for agricultural production and that 1.5 billion ha of land are currently being utilized for crop production (Hoang et al. 2023). As a result, agriculture is one of the activities engaged most frequently worldwide. To increase the amount of food that can be produced, approximately 2.7 billion ha of land may be utilized. Cereals, comprised of wheat, maize, rye, barley, millet, and sorghum, are the most cultivated crops across the globe. Rice is another important crop that is grown. The cultivation of cereal grains, including rice, maize, millet, barley, and wheat, takes up approximately two-thirds of the total agricultural land area. Other important crops that are cultivated on a global scale include oil palm fruit, cotton, canola, sugar beets, peanuts, potatoes, cassava, sunflower, rapeseed, and sugarcane. In addition to these types of crops, fruits and vegetables are also cultivated on a substantial scale worldwide. Apples, bananas, oranges, grapes, and mangoes are among the fruits that are produced the most frequently. For vegetables, tomatoes, potatoes, onions, carrots, and lettuce are among the most popular options. Animals such as cows, pigs, chickens, and sheep are produced for their meat, milk, and eggs, contributing to food production worldwide. Livestock production also plays a vital role in the global food supply. Farming of fish and other aquatic organisms, sometimes known as aquaculture, is an additional vital source of food for many people worldwide. In general, the variety of crops and livestock that are produced globally are a reflection of the myriad of agricultural practices and environmental conditions that exist in the world's various regions, as well as the multitude of dietary preferences and cultural traditions that exist among the people who live in those regions. As a consequence of this, they have contributed to the production of a significant quantity of AW all over the world (Kaushik and Sharma 2020).

AWs encompass all residues from the processing and production of agricultural yields (such as poultry, crops, meat, fruits, dairy products, and vegetables). They can be categorized into four categories. AWs are a problem in many countries across the world. The agricultural activities in fields directly generate waste materials, including stoves, straws, seedpods, and leaves. It is anticipated that 2802 million tons of crop residue will be produced annually worldwide. It is generally agreed that agricultural residues, created from crop residues, are the most abundant and least expensive form of organic waste. In addition, they can be transformed into a wide variety of products that have added value. The crops, as mentioned earlier, can be harvested at any time of the year; however, only a tiny percentage of them are used as fodder (Hoang et al. 2023).

In addition, crop residues such as oats, barley, and sorghum are included in the category of AW. As for the waste produced during agricultural product processing, agro-industrial waste can emerge from various activities, including the creation of nonfood agro-based products and processing of animal products and food items, among other things. These wastes can be produced at various stages throughout the manufacturing process. They can include byproducts such as fruit peels, vegetable scraps, starch residues, de-oiled seed cakes, and animal fat. Other examples of waste that can be produced include animal fat and scraps of vegetables. Recycling and reusing unwanted goods like these can reduce waste, conserve resources, and manufacture things that have increased value (e.g., *Pongamia pinnata* and *Jatropha curcas*).

Animal production is growing substantially, particularly in developing nations, as a direct result of an increase in the consumption of meat. Around 56 billion animals are bred and slaughtered yearly for human food and other products. It is anticipated that by 2025, this number will have increased by a factor of two, representing a more rapid growth rate than any other agricultural subsectors (Mohamed et al. 2021). The cattle business is primarily responsible for most of the current environmental issues, including GHG emissions, land deterioration, contamination of water and waste, and serious health concerns. However, environmental concerns and the worldwide rise in demand for meat have received less attention; a huge quantity of waste from livestock is hazardous to environmental hygiene and can have adverse effects on development if appropriate remedies are not provided. Therefore, it is vital to practice careful control of AW sources.

As observed, most agricultural residues include between 80% and 85% of lignocellulose contents. These components include lignin, cellulose, and hemicellulose. Biofuels derived from agricultural byproducts can be an effective means of reducing emissions and improving environmental sustainability. However, care must be taken to ensure its manufacture does not hurt the environment or deplete natural resources. The predominant constituents of animal waste primarily consist of cellulose comprises from 30% to 50% of biomass, hemicellulose ranges from 20% to 38%, and lignin ranges from 7% to 21%. Based on a comprehensive review of many sources, it has been determined that the composition of lignin, hemicellulose, and cellulose in agro-processing wastes can vary between 21% and 45%. In addition, the percentage of total solids (TSs) composed of carbohydrates in wastes from industrial processing plants fluctuates from 40% to 85%. Waste products from vegetables and fruits mostly contain carbohydrates, lipids, and proteins; their moisture levels can range from 80% to 90% (Chang and Hsu 2008).

The waste produced by processing fruits and vegetables contains high concentrations of various antioxidants, carbs, pectin, minerals, fiber, colors, and flavors. The phosphorus concentration can range from 9 to 280 mg L^{-1}, while the total nitrogen concentration can range from 14 to 830 mg L^{-1} in dairy waste. The preparation of meat can have a negative impact on the environment because the waste products from meat provide a suitable habitat for pathogenic bacteria. On the other hand, the high protein content of meat residues makes them a potential candidate for use in secondary biological therapies. The processing of marine foods and seafood also produces byproducts high in chitin, gelatine, proteins, and chitosan. The COD and BOD values of poultry waste are relatively high because feathers, skin, and blood all contain large amounts of carbohydrates, lipids, and proteins. The carbohydrate content of animal wastes ranges from 50% to 60%, making manure an ideal source for biogas. When estimating the biogas potential of different types of AW feedstock, the concentrations of lipids and proteins play a pivotal role.

AW is one of the world's most plentiful and ever-present renewable energy sources. Because large quantities of biomass produced as agro-by-products pollute the environment, the waste generated by these processes must be managed efficiently to prevent further damage to the natural world. Developing valuable goods and lessening the harmful effects of waste on the surrounding environment are potential outcomes of effectively exploiting agricultural byproducts and waste. To accomplish this goal, it is essential to devise and implement WM strategies that are kind to the environment and cut down on waste production, increase waste reuse and recycling, and transform waste into products that can be used. Composting, anaerobic digestion, biorefineries, and utilization of AW in energy production through gasification and pyrolysis are a few examples of the solutions that fall under this category. These solutions assist in garbage management and contribute to sustainable development by lowering environmental pollution, preserving natural resources, and bolstering economic expansion (Rautela and Kumar 2021).

Agriculture generates waste, but it is not the sole source. Food chains and other agricultural practices can produce solid AW. At each point of the food chain, waste will occur. These consist of the following (Fig. 17.1):

(a) *Food and Meat Preparation*: Abattoirs generate waste from crop and animal production. Therefore, bones, banana peels, feathers, and hooves are solid wastes.
(b) *Horticulture*: These solid wastes result from the aesthetic maintenance and growing of plants. Essentially, they play a larger role in gathering than in farming. The waste is caused by trimming and mowing.

Food and Meat Preparation

Horticulture

Production of Animals/Livestock

Plant Production

Wastes from Industrial Processes

On-Farm Healthcare

Fig. 17.1 Various components of agricultural waste

(c) *Production of Animals/Livestock*: Animals will inevitably generate solid waste. If cattle are used in agriculture, animal manure, water, troughs, and animal carcasses will be used.

(d) *Plant Production*: Crop production does result waste, such as crop leftovers and husks. This occurs while cultivating plants for food or domestic purposes.

(e) *Wastes From Industrial Processes*: Agriculture generates industrial raw materials and residential goods besides food production. Consequently, they result in waste. Utilizing agricultural materials, paper manufacturing generates waste. In addition, wood cutting and processing produce it.

(f) *On-Farm Healthcare*: Due to the usage of medications, vaccines, and insecticides on animals, this waste has occurred. Vaccine needles, syringes, and packaging contribute to this problem.

(g) *Chemicals*: This is one of the most prevalent forms of agricultural land waste. Pesticides, herbicides, insecticides, and improper usage of synthetic fertilizers can all contribute to environmental pollution. Farmers, for instance, do not empty herbicides and insecticides but rather mishandle the containers and spill these chemicals into surrounding ponds or fields. This results in environmental hazards, food poisoning risks, and water contamination, causing harm to humans, animals, and marine life.

Further frequent wastes include kitchen waste, organic fertilizer bags, zero-waste oil, manure, etc.

17.3.1 Wastes from Farming Activities

Although a tropical climate is conducive to the growth of crops, it also promotes the germination and development of plant-eating weeds and pests. This scenario leads to a high demand for pesticides, which are required to kill insects and prevent the spread of epidemic diseases; as a result, farmers habitually abuse chemicals in their crops. In tropical locations, pesticides are routinely employed to manage weeds and pests that might damage crops, but their misuse can adversely affect the environment and human health. When pesticides are used excessively or improperly, they can pollute the soil, water, and air, causing harm to nontarget creatures such as beneficial insects, birds, and fish. In addition, pesticide overuse can lead to the evolution of pesticide-resistant insects, making it more difficult to control subsequent infestations. Thus, it is crucial to promote the safe use of pesticides and stimulate the development of alternative pest control strategies to limit the hazards associated with their usage (Kaushik and Sharma 2020).

Furthermore, improper pesticide packing and container disposal can have substantial environmental consequences. If these canisters containing pesticide residues are burned, they can contaminate land, water supplies, and air. This contamination can have negative consequences on the health of humans, animals, and plants and lead to the emergence of pests and weeds that are resistant to the substance. In addition, burning pesticide containers can emit harmful chemicals into the air, adding to air pollution and potentially damaging the respiratory health of local communities. In order to limit the risk of environmental pollution and human health issues, it is vital to implement correct disposal and recycling processes for pesticide containers. This is due to the potentially toxic substances they contain, which can be persistent. Existing pesticides that are either unused or have become stagnant, as well as pesticide packaging that still contains residue from the original contents, pose a significant risk to the environment. This is because these substances could be improperly stored or buried, which would cause them to leak or enter the environment through osmosis, thereby causing damage to the environment. When it comes to the production of food, fertilizers play an extremely important role. For instance, they ensure that plants continue to be productive and of high quality. Inorganic fertilizer is inexpensive and produces significant plant growth (Ramachandran et al. 2007). Despite this, most farmers use significantly more fertilizer on their crops than the plants need. To increase annual agricultural output, an excessive amount of fertilizer is applied, which results in the fertilizer being abused to the point that it is misused. The absorption rate of these fertilizer compounds (nitrogen, phosphorus, and potassium) is influenced by the soil conditions, kind of plant grown, and fertilization techniques used. A portion of the excess fertilizer either stays in the soil; causes surface water pollution as a result of its entry into ponds, lakes, and rivers as a result of surface runoff or the irrigation system that was used; causes groundwater pollution; or causes air pollution as a result of its evaporation or de-nitrification.

17.3.2 Waste from Animal Production

Livestock activities generate solid waste such as dung and organic materials in slaughterhouses: liquid waste such as urine, cage wash water, waste from washing animals and maintaining hygiene in slaughterhouses; air pollutants such as H_2S and CH_4; and odors. Since most livestock farms are often situated close to residential areas, the ensuing pollution is a significant issue. Air pollution includes odors from cages due to the digestion of livestock wastes and the putrefaction of organic matter in manure, animal urine, and spoiled foods. With manure and other wastes being discharged into water bodies, livestock production can also contribute to water contamination. This has the potential to contaminate drinking water supplies and destroy aquatic life. Introducing antibiotics and hormones into water sources from livestock feed can also contribute to water pollution. In addition, the disposal of animal corpses and slaughterhouse wastes can constitute a considerable WM burden. These materials can be a source of infections and other dangerous compounds; therefore, their disposal must be adequately handled to prevent adverse effects on human health and the environment (Jaleel et al. 2010). These aromas contribute to the degradation of the quality of the air. The number of animals present, as well as the ventilation, temperature, and humidity, all impact the potency of the stench. The different phases of digestion, organic materials, food components, microbes, and animal's overall health all contribute to differences in the amounts of NH_3, H_2S, and CH_4 produced by the animal. This source of waste, which has not been treated and cannot be recycled, can release GHGs, have a detrimental impact on soil fertility, and contribute to water contamination. About 75–95% of cattle waste is water, while the remainder consists of organic debris, inorganic stuff, and numerous kinds of bacteria and parasite eggs. These microorganisms and chemicals can transmit disease to humans and have several detrimental environmental consequences.

17.3.3 Waste from Aquaculture

The growth of the aquaculture industry has resulted in a greater need for feeds designed to boost production. The quantity of feed consumed within a system is the factor that has the greatest impact on the amount of waste generated by the system. In this part of the investigation, the waste from aquaculture feeds is analyzed and discussed (Zorpas 2014). The metabolic waste created by aquaculture can either be dissolved or suspended, and it is one of the most significant wastes produced. Approximately 30% of the feed used on an effectively managed farm will be discarded as solid waste. The temperature of the environment affects the rate of feeding. A rise in temperature causes an increase in feeding, which increases waste production. Water flow patterns in production units are crucial for WM because they limit fish feces' fragmentation and facilitate the settling and concentration of settleable materials. Water flow patterns in manufacturing facilities are essential for waste control. The patterns of water flow in aquaculture production units can have a substantial effect on WM. Appropriate water flow patterns can aid in minimizing the fragmentation of fish excrement and other organic debris, hence facilitating the quick sedimentation and concentration of settleable materials. This can facilitate the removal of solid wastes and avoid the excessive accumulation of organic matter, leading to water quality difficulties and other problems. In addition to maintaining oxygen levels, preventing the accumulation of toxic substances, and promoting healthy fish growth, good water flow patterns can assist in sustaining oxygen levels (Tokarchuk et al. 2021). This can be very important since a significant portion of the excrement that has not been fragmented can be collected right away, which will result in a substantial reduction in the amount of organic waste that has been dissolved.

17.4 System of Agricultural Waste Management (AWMS)

AW management, abbreviated as AWM, has recently garnered the attention of policymakers as an issue important to ecological agriculture and sustainable development. Historically, the typical approach for removing waste from agriculture has been to release it into the surrounding environment, with or without treating it first. It is vital to regard wastes as potential resources rather than as undesired and unwelcome to avoid the pollution of air, water, and land resources and prevent the spread of harmful materials. This is necessary to avoid the spread of dangerous materials. This will require a shift in thinking and attitudes, improved ways to manage AW, and enhanced strategies for using technology and incentives. Organic wastes, particularly animal manure, have the potential to dramatically impair the quality of soil, water, and air if they are not handled properly or if they are not treated in any way. Flies use stagnant wastes as a breeding environment, which makes these wastes a vector for the spread of disease (Mishra et al. 2016). The uncontrolled breakdown of organic wastes generates odorous fumes and ammonia volatilization, resulting in acid rain. There are several concerns regarding:

- Water quality as a result of higher nitrogen and phosphorous loadings.
- Pathogens and antimicrobial compounds in manure.
- Foul odors and air quality as a result of ammonia, methane, and nitrous oxide emissions.
- Soil quality as a result of potassium and phosphorous loading.

To maintain or improve the quality of air, water, soil, plant, and animal resources, an Agricultural Waste Management System (AWMS) must be “a designed system in which all necessary components are established and managed to control and utilize byproducts of agricultural production.” In other words, the entire spectrum of AW, from harvest to table scraps, may be stored and processed in this system, which was designed with a year-round, holistic system approach in mind (Rathore et al. 2022). The best course of action for dealing with AWs is determined by their TS concentration. Climate, animal species, amount of water taken by the animal, and type of

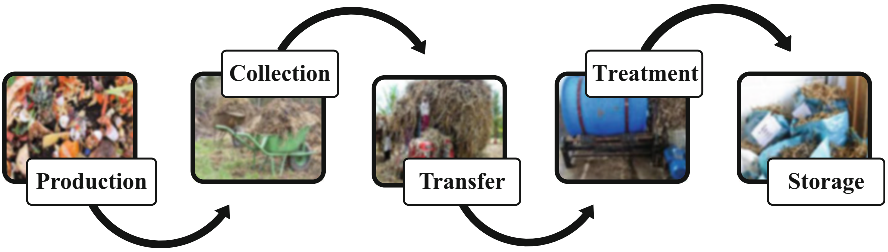

Fig. 17.2 Agricultural waste management functions

feed all affect the concentration of TS in expelled dung. Most setups can predict or quantify waste regularity. Adding bedding or other solid waste can raise the waste's TS concentration, while adding water can lower it; prohibiting further water addition can stabilize it. The concentration of TS is crucial since it affects the total amount of waste that needs to be handled.

Though initial investment in liquid-handling equipment could be more than that in solid waste handling, automated and managed liquid WM systems are more common. The six core roles of AWMS are summarized in Fig. 17.2, which are production, collection, storage, treatment, transfer, and usage. The output is sensitive to the nature and volume of AW. If there are enough for it to be a resource problem, the waste needs to be controlled. When analyzing production, it is important to consider the kind of waste produced, how often it occurs, how much there is, where it is, and when it occurs. The AWMS strategy should outline what constitutes AW and how it will be generated, used, and managed. Factors to consider include the type of collection used, where and when it will be performed, how many people will be needed, what kind of infrastructure will be required, how much it will cost to manage and install, and how much the waste will change in composition as a result of the collection. Waste is temporarily contained or held in storage for the sake of convenience. Because activities like waste treatment and disposal can be delayed by inclement weather or impeded by competing activities, the WM system's storage facility controls the system's schedule and timeliness. The WM system should identify many factors related to storage, including the period of storage, the required volume of storage, the type of storage facility, the expected size of the facility, its location, and the installation cost. Additionally, the system should determine the management cost associated with the storage process and assess the impact of storage on the consistency of the waste. Physical, biological, and chemical processes are all treatment methods that aim to minimize waste's negative environmental impact while maximizing the material's reusability. Activities like analyzing the waste's characteristics before treatment; deciding what those characteristics should be after treatment; choosing the type, size, and location; estimating installation cost; and budgeting for treatment management are all part of the pretreatment phase. Depending on the TS content, waste is transported from the collection stage to the use stage as solid, liquid, or slurry. Recycling useable waste and releasing nonbiodegradable waste back into nature are examples of the utilization process.

Many bioactive compounds can be found in agricultural byproducts. Biogas, biofuel, mushrooms, and tempeh are some products that may be made using these wastes as an alternative raw material source. Costs in manufacturing and pollution to the natural world can be reduced by using agro-industrial waste products as raw materials. Producing biofuels, enzymes, vitamins, antioxidants, animal feed, antibiotics, and other chemicals from agro-industrial wastes is accomplished by solid-state fermentation (SSF). A wide range of microorganisms is used in SSF processes to generate these valuable compounds. The significance of SSFs in manufacturing high-quality goods is discussed and analyzed (Satyanarayana Reddy et al. 2021).

The majority of waste products are produced by agricultural industries every year. Improper disposal of these waste products could lead to environmental pollution and harm human and animal health. Most publications state that incineration, dumping, and unplanned landfilling are the primary disposal methods for untreated and underutilized agro-industrial wastes. Increases in GHGs are just one way these untreated wastes contribute to various climate change problems (Zakaria et al. 2020). Furthermore, the combustion of fossil fuels is a major source of GHGs. Therefore, it is a worldwide challenge to create bioenergy sources that are considered as alternative, are cleaner, and can be used for a long term. There is a serious problem with how these wastes can be disposed of. For instance, the production of juice results in a large amount of waste in the form of peels, coffee shops generate waste in the form of coffee pulp, and cereal factories generate husks. The expected amount of wheat straw residues in the 1990s was 709.2 million metric tons, while the amount of rice straw residues was predicted to be 673.3 million metric tons. These agro-industrial byproducts are being given increased attention for quality control because of the high nutritional potential implied by their composition.

Many types of waste, including pomegranate peels, lemon peels, and green walnut husks, can be used as natural antimicrobials. Wastes from organic compounds threaten the atmosphere, but they could be used to produce mushrooms as food and other bio-based goods such as bioenergy and biofertilizers. Some AWs are used to feed animals. However, the content of such waste varies widely; sometimes, it contains much protein and many carbs and minerals. Rather than being thrown away, these scraps can be used as a source of nutrients in manufacturing other goods. Raw materials provide an ideal environment for the growth of microorganisms due to these nutrients' presence. These microbes may convert waste materials into usable products. The byproducts of the agro-industrial sector provide robust support for the advances in SSF that enable the manufacturing of a wide range of useful products. It also helps produce fermentable sugars by making their reliance on staple crops cheaper. An extensive series of experiments were conducted to ascertain the efficiency with which various bacteria might convert AW into sugars. The possible applications of agro-industrial wastes through SSF processes were discussed to round up this review.

17.5 Agro-Industrial Waste Types

17.5.1 Agricultural Residues

Figure 17.3 depicts two types of agro-industrial waste: agricultural and industrial waste. There are two main types of AW: field residues and processing residues. Field residues are the leftover material on a field after harvested crops. Field remnants include leaves, stalks, seed pods, and stems, whereas processing leftovers include broken-down plant matter. Wastes such as molasses, husks, bagasse, seeds, leaves, stem, straw, stalk, shell, pulp, stubble, peel, roots, etc. can be put to good use in a variety of settings, including animal feed, soil improvement, fertilizers, manufacturing, and more. However, most of the time, agricultural byproducts end up in landfills. Managing and reusing farm waste are good ways to reduce water usage and erosion. Wheat and barley are the two most important cereal crops in the Middle East. Rice, lentils, maize, chickpeas, fruits, and vegetables are only a few crops farmed worldwide. The availability and characteristics of AW set it apart from other solid fuels like charcoal, wood, and char briquettes. However, industrial wastes result from the commercial processing of food products. Byproducts such as bran, bagasse, and press cake are produced as waste while manufacturing sugar, oils, and grains. Wastes from manufacturing biofuels like biodiesel and ethanol are also considered industrial leftovers. These scraps have the potential to be used as fuel, animal food, or even gardening material after undergoing appropriate processing. Sustainable development, environmental protection, and financial gain are all possible outcomes of improved agricultural and industrial residue management and usage.

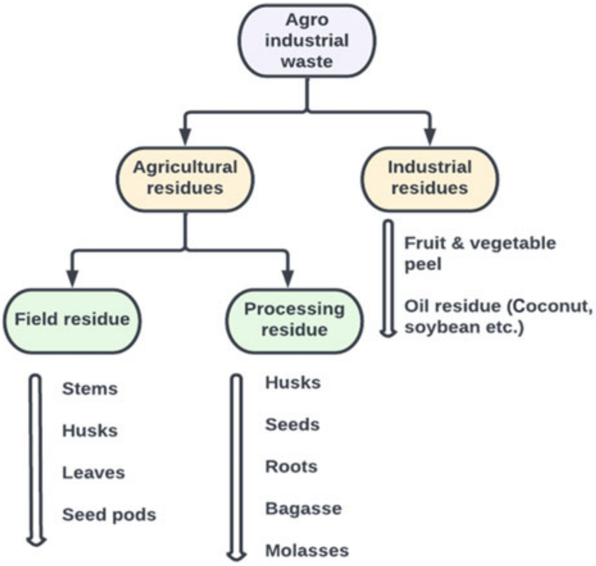

Fig. 17.3 Types of agro-industrial wastes

17.5.2 Industrial Byproducts

Large volumes of organic wastes and associated effluents are produced annually by enterprises in the food processing industry, including the juice, chip, meat, confectionary, and fruit industries. These biological waste products have numerous energy applications. The need for food and its various uses is increasing alongside the world's population. Therefore, in most nations, the food and beverage industries have grown substantially to accommodate the rising need for food. Cellulose, hemicellulose, lignin, moisture, ash, carbon, nitrogen, etc. are among the many components of fruit industry waste. These components might be biochemically broken down to produce things like biogas and bio-ethanol, which have commercial values. India produces a lot of apples, cotton, soybeans, and wheat, yet almost 20% of its yearly fruit and vegetable production goes to waste. Therefore, the percentage of waste produced by the country increases with its rising output. As in other types of industrial waste, BOD, COD, and other suspended particles are found in high amounts of food waste. Most of these wastes are either not utilized or not treated, which has detrimental effects on the environment and human and animal health. However, the composition of these wastes contains many organic compounds that produce various products with increased value and decreased production costs.

Large numbers of oil cakes, a byproduct of oil extraction from seeds, are produced in the oil industry. Due to the high quantities of fat, oil, grease, suspended particles, and dissolved solids in their waste, these enterprises are major contributors to air, water, and solid waste pollution. Oil cakes can range in composition depending on their foundation. Cakes made using canola oil, sunflower oil, coconut oil, sesame oil, mustard oil cake, palm kernel cake, soybean cake, groundnut oil cake, cotton seed cake, olive oil cake, and rapeseed cake are all distinct forms of oil cake. These stated agro-industrial leftovers are generally inexpensive and possess a high concentration of elements with boundless potential for consumption as alternative substrates for fermentation.

The nutritional composition and bioactive substances in agro-industrial wastes and residues are rich. Because these wastes contain a wide array of components, including carbohydrates, minerals, and proteins, referring to them as "raw materials" rather than "wastes" when discussing their use in other industrial processes is more accurate. The existence of such nutrients inside these wastes provides an environment that is favorable to the phenomenal growth of microorganisms. Waste products can be used as a source of nutrients for the growth of bacteria when the fermentation process is carried out. The solid support required for synthesizing a wide variety of valuable compounds can be provided by agro-industrial wastes, which can then be used in SSF processes. The recycling of waste and the overall greening of the environment have been aided by using waste products from agricultural and agro-based industries as raw materials. This practice can help reduce manufacturing costs.

The agro-based industry is an industry that adds value to agricultural raw materials through processing to create marketable and useful goods that generate profits for the producer. The agricultural sector includes the textile, sugar, paper, and vegetable oil industries. These enterprises allow effective and efficient agricultural raw material utilization. The agriculture sector accounts for around 17% of our nation's gross domestic product, which gives these industries a substantial footing in our country (Wong et al. 2016). It results in the diversification and commercialization of agriculture, increasing farmers' earnings and generating food surpluses.

On the other hand, India generates over 960 million tons of solid waste annually as byproducts of industrial, mining, municipal, agricultural, and other processes. However, the term "waste" is inappropriate because these residual parts have a high nutritional value and can be used as raw material to produce other products such as fertilizer, animal feed, soil improvement, etc. This raw material consists primarily of husks, molasses, seeds, bagasse, straw, stem, leaves, stubble, peel, and roots (Idowu and Schmidpeter 2022). The phytotoxicity test revealed that agricultural residues are abundant in bioactive chemicals and devoid of phytotoxic substances. Composting can biodegrade and stabilize the organic substrates in solid waste, and the resulting compost products can be put on land as fertilizer or soil conditioner.

17.6 Utilization of Agricultural and Industrial Wastes

Composting is a controlled procedure using natural microbes in organic matter and soil to degrade organic wastes. For breakdown, these microbes require sufficient basic nutrients and oxygen. Methane gas can be produced from the waste products of agricultural operations, notably manure, through a process known as anaerobic digestion. This gas is an excellent choice for heating applications, such as barbecuing, heating water, drying grain, and similar tasks. In pyrolysis systems, AW is burned at temperatures ranging from 400 to 600 °C in the absence of oxygen to cause a portion of the material to evaporate, leaving behind a char. This practice is a cutting-edge approach to exploiting waste from agricultural production. Animal feeds and crop leftovers have a high fiber content but low protein, carbohydrate, and fat content. As a result, the traditional method of increasing meat output, which consists of supplementing grass and pasture with grains and protein concentrate to boost livestock numbers, might not satisfy the expected growth in demand for meat proteins. Direct combustion is one of the oldest technologies for converting biomass into usable energy. All that is required to complete the process is to use waste products from agricultural production as fuel. The full combustion of AW entails a rapid chemical reaction, known as oxidation, between biomass and oxygen, the release of energy, and the simultaneous generation of the end products of organic matter's oxidation, carbon dioxide, and water (Thakur et al. 2020).

Agro-industrial waste is the leading cause of water and lake contamination. Chemicals from fertilizers and pesticides wind up in groundwater and are then consumed. There may be health concerns as it contributes to the blue baby syndrome, the leading cause of infant mortality. Fertilizers, manure, waste, and ammonia convert to nitrate, which limits the amount of oxygen in water, causing the death of aquatic organisms.

17.7 Centralized Approach for Agricultural Waste

Globally, there are two systems for managing municipal solid waste: centralized WM and decentralized WM. In some places, on the other hand, there is a hybrid method that combines elements of each of the methodologies above. The term “centralization” refers to the organizational structure in which all decision-making authorities is placed in the top management, and all subordinates are compelled to follow the directions of their superiors. This type of structure is known as a “top-down” structure. The centralized system often entails extensive infrastructures, necessitating more space and additional cash to transfer and manage municipal solid waste. During the first stages of the planning process, an appropriate WM strategy needs to be chosen. When policymakers prepare for a WM solution, they pay much attention to enhancing technical specifications but typically disregard the larger social and ecological objectives.

While developing WM, rather than concentrating solely on technological progress, a social component such as “public engagement” is incorporated. In such a circumstance, the WM strategy may become more sustainable due to increased citizen knowledge of environmental issues. According to the “Manual on Solid Waste Management Systems,” centralized WM has advantages over economies of scale, a single monitoring point, advanced technology, and environmental controls. However, the downsides of a centralized approach to WM must also be considered. For instance, establishing and maintaining a centralized WM system can be expensive, particularly in developing nations. However, ensuring that waste is collected and transported efficiently and properly can be challenging, which can result in environmental and health risks. In addition, the centralized approach may not always account for local communities’ specific demands and conditions, which can result in a lack of community engagement and participation in WM activities. Hence, combining centralized and decentralized WM strategies may be more effective and sustainable over time. This is according to the comparison of the strengths and weaknesses of the two techniques. On the other hand, researchers have uncovered a few advantages of the decentralized technique that focus on individuals, such as the following:

- Transport over short distances; because waste only needs to be transported over short distances, this reduces the amount of money spent on transport and the amount of pollution caused by the emission of air pollutants, noise from cars, and amount of road traffic.
- A decrease in the amount of space needed to store biodegradable waste; typically, biodegradable waste is handled at the point of generation through a decentralized manner, shortening the time it must be stored. This technique will produce disagreeable odors less frequently, reducing the spread of disease-causing vectors.
- Advantages for the surrounding neighborhood and community; the possibility of the system having negative effects on neighboring individuals in terms of loss of

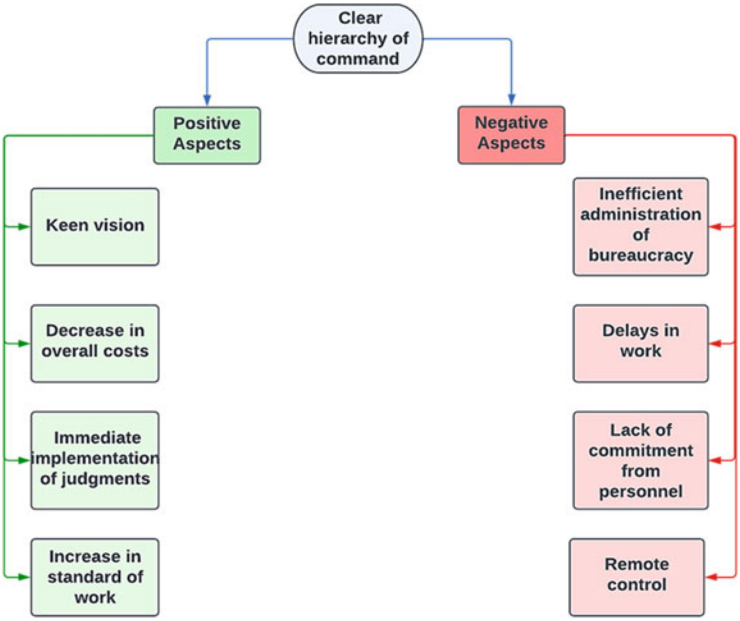

Fig. 17.4 Positive and negative aspects of centralized approach to waste management

livelihood and ecological degradation is reduced due to the smaller structure sizes and lower volumes of waste handled in decentralized facilities.

The process of an organization's planning and decision-making operations becoming centralized under the direction of a single individual or location is referred to as centralization. When an organization is centralized, the decision-making authority is retained by the head office, while all subordinate offices are responsible for carrying out the head office's directives. All the experts and executives who make decisions are in the headquarters. Likewise, in a centralized government system, the authority to make decisions is centralized at the highest level, and all lower levels must comply with instructions issued by the highest level (Fig. 17.4).

17.7.1 The Positive Aspects of Centralized Control

The following are some of the benefits that come with effective centralization:

- A Clear Hierarchy of Command at All Levels
  Because there is a defined chain of command, each member of a centralized organization knows to whom they should report. When they have questions or concerns about the company, junior employees know whom to approach. On the other hand, senior executives adhere to a well-outlined structure when delegating

authority to staff members with expertise in particular responsibilities. When the leaders delegate responsibilities to lower-level managers and other employees, they enjoy the peace of mind that there will be no unnecessary duplication of efforts. It is beneficial for an organization to have a clear chain of command, particularly when it must implement decisions rapidly and in unison.

- Keen Vision
  When a corporation has a centralized management structure, it is much simpler for that company to carry out the strategies outlined in its vision. Because there are open lines of communication, the senior executive can communicate the aim of the business to the staff members and aid them in working toward realizing that goal. There will be inconsistencies in communicating with employees because there are no established lines of power in the absence of centralized administration. This will generate communication issues. The organization's vision should be directed downward from the top, making carrying out its objectives and concepts easier. In addition, the organization's stakeholders, such as customers, suppliers, and communities, hear a consistent message from the business.
- A Decrease in Overall Costs
  A centralized company is more likely to adhere to standard operating procedures and methodologies, reducing the costs of office and administrative work. Because all the most important decision-makers are in the company's headquarters, sending different departments or equipment to the other offices is unnecessary. Because significant choices are taken at the center and communicated to the branches, the company does not incur additional costs to engage specialists for its components. In addition, this means that the company saves money. The short chain of command helps reduce the overlap of responsibilities, which allows the company to avoid incurring unnecessary additional costs.
- Immediate Implementation of Judgments
  In an organization with a centralized management structure, decisions are made by a select few persons, who then communicate their choices to management at lower levels. When only a few persons are engaged in the decision-making process, it is easier for them to discuss the particulars of each alternative in a single meeting, making the process more efficient. After that, the decisions are communicated to the subordinate levels of the organization so they can be implemented. Involving managers at lower levels in the decision-making process will cause it to take longer and result in a greater number of conflicts. Because of this, the implementation process will take longer and be more complicated than it would have been otherwise because some managers may challenge the decisions if their input is neglected.
- Increase in the Standard of the Work
  Greater job quality is achieved in centralized companies through standardized processes and increased levels of control. The outputs of each department are supervised by individuals who ensure that they are consistent and of high quality. Using contemporary technology helps reduce the potential for waste caused by human labor and contributes to maintaining a high level of work quality. The

standardization of work reduces the duplication of tasks, which in turn helps reduce the costs associated with labor.

17.7.2 Drawbacks of An Overly Centralized System

The following is a list of the negative aspects of centralization:

- Inefficient Administration of Bureaucracy
  Regarding leadership, centralized management is very similar to the authoritarian style. In centralized management, employees are expected to give just the outcomes the top executives have allocated. It is not possible for employees to participate in the company's decision-making process; rather, their role is limited to that of implementers of decisions made at a higher level. Executives are only responsible for making decisions; they are not responsible for putting those decisions into action; thus, they will not understand when employees struggle to make particular decisions. Because workers lack the motivation to make decisions by upper-level managers without input from lower-level employees, the organization's performance suffers as a direct result of these activities.
- Remote Control
  The organization's executives are under incredible pressure to make decisions, even though they do not influence the implementation process. Because they have not decentralized the decision-making process, chief executive officers (CEOs) have significant additional work to complete. The executives do not have sufficient time to oversee the decisions' implementation. The upshot of this is that the employees are hesitant. As a result, CEOs may make excessive decisions, many of which are either poorly implemented or ignored by staff members.
- Delays in Work
  The task is delayed due to centralization as it requires records to be sent to and from the main office. If there is a delay in conveying the documents to the workers, who rely on the information communicated to them from the top, there will be a loss of person-hours. This suggests that workers' overall productivity will suffer if they are required to wait extended periods for direction on the tasks that come after them.
- A Lack of Commitment from the Personnel
  Employees who are allowed to demonstrate initiative in their work are more likely to remain loyal to their employer. They can present their uniqueness and propose strategies for achieving particular goals. On the other hand, when tasks are centralized and decided by top executives, there is little room for employees to exercise their initiative in the workplace. The regimentation of the task hinders their capacity for creativity and dedication to the organization. Centralization is a management style in which the power to make decisions is concentrated in a small group of executives at the top of the organizational structure. Senior management is responsible for making decisions, which are then communicated to lower-level managers.

It should be emphasized that the decentralized MSWM method would call for increased time spent on the planning phase to achieve consensus among all relevant stakeholders. In addition, the municipal authority's role in the decentralized MSWM plan is limited to that of a facilitator. The municipality takes on most WM responsibilities under a centralized MSWM system. These responsibilities include collection, transportation, treatment, and disposal of waste.

Sustainable WM necessitates the use of various management systems to restrict waste production, optimize energy and material recycling, and satisfy economic, environmental, and social sustainability objectives. It may be beneficial to implement a semicentralized strategy for managing specific waste types, such as treated sanitary waste, biomedical waste, and inorganic waste storage, in addition to adopting a decentralized strategy as the primary focus of one's efforts and making its implementation a top priority. Even within the framework of semicentralization, there exists a decentralization component at the source level (Rathore et al. 2022). This decentralization component is the essential element that ensures the success of centralized WM. On the other hand, the state government is considering constructing "centralized waste-to-energy (WtE) plants" to generate electricity from MSWM. The biowaste produced in Kerala has a low calorific value, which means that its incineration would not yield high energy. This is one of the reasons why the majority of waste-to-energy plants that have been built in India have been unsuccessful.

Experts in "zero waste" say this is the case. The term "integrated solid waste management" can be formed by combining the ideas of decentralized municipal solid waste management (MSWM) and centralized MSWM (as restricted means of treating sanitary waste, biomedical waste, and inorganic waste) (Hiloidhari et al. 2020). The idea of "integrated solid waste management" is founded on the assumption that the waste stream is composed of distinct components and that each waste should be disposed of individually; as a result, the concept of segregation is of utmost importance. This is because the waste stream is assumed to have distinct components. In integrated solid WM, equity, effectiveness, efficiency, and sustainability are considered to be the four most basic ideas. Everyone should be able to get their hands on a suitable WM method, considering the environmental worries and people's health. The selected WM process should result in securely removing all sorts of waste. The model for the management of waste should be established in such a manner that its advantages are maximized while its expenses are reduced to a bare minimum. In other words, the model should be developed in such a way that for the sake of sustainability, the WM system needs to be adapted to the specifics of the area in question and to be workable from a variety of perspectives, including technical, environmental, social, economic, monetary, institutional, and political perspectives (Singh'nee Nigam and Pandey 2009. In addition, its continued existence should not exhaust the resources upon which it relies. With the decentralized method, "integrated sustainable waste management" considers the municipal body and other stakeholders, such as waste generators and formal and informal organizations connected with WM.

It is a challenging problem that needs to be examined before the system can be put into place, and selecting the best method for managing organic AW is one of those problems. In addition, much research on developing and growing nations have concluded that a lack of collection and processing facilities is the root cause of nonsegregation and a poor collection rate. Several studies have given facility allocation methodologies and determined the locations of MSW collection and transfer facilities in metropolitan areas. These facilities are located in cities. Several studies have concentrated their attention on the path collection vehicles take to enhance the effectiveness of collection efforts. The location of composting plants for organic municipal solid WM can also be determined with the help of these facility allocation models, which can be utilized in both cases. In addition, the path that waste collection vehicles take is an important factor in determining the long-term viability of AW management (Rathore et al. 2022).

Regarding the research on facility allocation and WM in connection to AW, these are all crucial factors to examine. On the success of WM strategies, variables such as income levels, waste segregation participation rates, and environmental and social costs can have a considerable impact. Researchers can contribute to the existing literature on facility allocation and WM by considering these variables. For instance, they can assist in determining the most efficient facility allocation techniques for various forms of AW and communities with differing economic levels. They can also contribute to the development of more efficient waste collection route plans, reducing the environmental and societal costs of WM. In addition, by investigating the safety issues involved in controlling unpredictable waste generation, researchers may reduce the hazards connected with WM and ensure that the process is safe and sustainable. By examining the costs associated with inconvenient AW disposal, researchers may promote increased participation in waste segregation and guarantee that waste is managed responsibly and sustainably. These variables contribute significantly to our understanding of facility allocation and WM regarding AW.

17.8 Treatment of Agro Wastes

Many applications can be found for diverse types of AW because these wastes have distinct physical and chemical compositions or properties. The geographical location and the nature of the economic activity inside the region may affect eligibility. Because AWs contain a significant amount of organic matter, they are typically put to better use as compost or feed for animals than as fuel. Other substances, including cellulose, hemicellulose, and lignin, are AWs and can be incorporated into producing chemicals, resins, and enzymes. It is anticipated that surpluses will occur, and those surpluses can be transformed into solid fuel briquettes. This is the case even though some applications have prioritized certain agricultural byproducts. Composting, making animal feed, and producing biogas and briquettes are the four primary ways to process acceptable AW (ABBC technologies). These technological advancements can be made in response to demand and specific requirements. In theory, three approaches to recycling AW might be best for developing communities. Some examples of these products and processes include animal feed, energy in the form of solid briquettes or gaseous biogas, and land reclamation

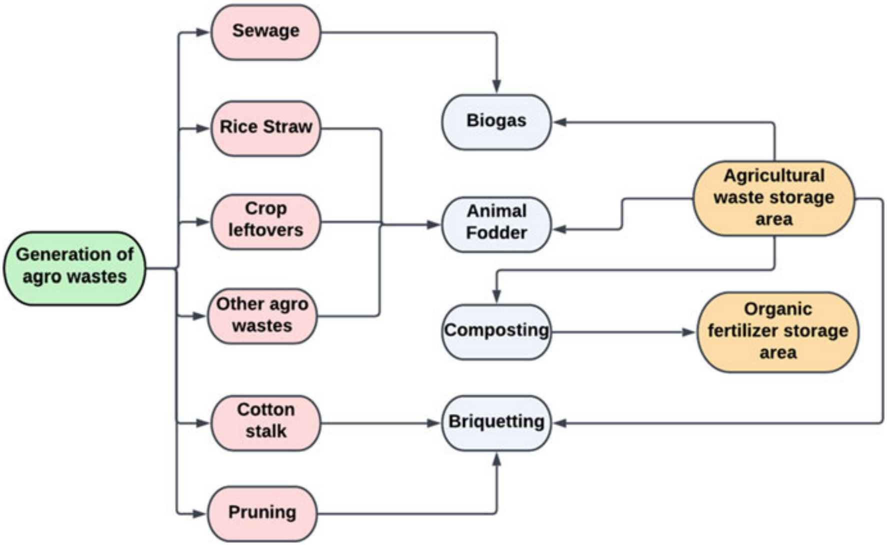

Fig. 17.5 Technology used for the treatment of agricultural waste

through composting (Gupta et al. 2022). Other methods, such as gasification, fiberboards, chemicals, silicon carbide, pyrolysis, etc., may be suitable for certain countries depending on their requirements, but these methods are not universally applicable (El-Haggar 2007).

The quantity of waste produced by agriculture differs from nation to nation depending on the crops grown and the total area farmed. This waste occupies agricultural grounds for days and weeks until farmers dispose of it by burning it in the fields or keeping it on the roofs of their homes, both of which have a negative impact on the environment by allowing diseases to spread and fires to start. This waste also occupies agricultural grounds for days and weeks until farmers burn it in the fields or keep it on the roofs of their homes. The most significant contributors to most of these agricultural pollutants are the crops of rice, wheat, cotton, and corn crops. After conducting the study, it was concluded that these crops would benefit most from utilizing three distinct approaches to recycling AW. The first method is animal fodder, which improves AW's digestibility and nutrient content to make it suitable for animal consumption. This process can be used to feed animals. The second technology is energy, which can generate power from either solid (by briquettes) or gaseous (by composting) AW (biogas). Briquetting, a method that transforms AW into briquettes, can be exploited as a viable fuel for furnaces in domestic and industrial settings (Fig. 17.5).

AW and urban garbage can be combined through the biogas process to produce biogas, organic fertilizer, and energy. Composting is yet another method for converting organic waste into soil conditioners, which can later be converted into organic fertilizer. To ensure that AW is efficiently utilized, employing a complicated combination of these strategies is necessary. This can aid in addressing the obstacles rural communities face and encourage sustainable development. The nature and properties of AW can vary considerably; therefore, it is essential to construct a collection system that can efficiently collect and transport the waste to the complex. Once reaching the facility, the waste can be shredded and processed to generate a steady supply of AW for the system. By altering the carbon-to-nitrogen ratio and the amount of water in the waste, the complex can help rural communities handle their problems and promote the sustainable use of AW. This can aid in producing various useful products, such as compost, animal feed, briquettes, and energy. Overall, a complicated approach combining biogas processing, composting, and other techniques can aid in efficiently utilizing AW and promoting sustainable development in rural communities.

17.9 Challenges and Perspectives for Future Research

The amount of AW that contributes to the overall waste is around 15%. Because of this, the efficient management of AW offers one of the greatest challenges because it affects the economy's operation and the day-to-day activities inside it. The environment is harmed and valuable resources squandered as a direct result of the massive amounts of biomass collected annually in the form of byproducts (e.g., bioactive compounds and chemicals, fuel, feed, and food). As a consequence of this, it is necessary to put into practice a variety of eco-friendly strategies for the management of waste. Valorizing AW is an essential technique for managing AW, as it transforms waste into useful and valuable goods. This can be accomplished in several ways, including biorefining, which involves the conversion of biomass into high-value goods, and bioenergy production, which involves using waste to generate energy. The valorization of AW may also involve manufacturing bio-based products, such as biofuels, bioplastics, and bioactive chemicals, which can be utilized in various applications, such as fuel, food, and medications. Valorizing AW is crucial for reducing waste and generating new prospects for economic development and sustainability (Hoang et al. 2023). Valorization can be performed on a variety of wastes, including AW. Even though the valorization of AW is seen as an appealing strategy for achieving sustainability, there are still significant challenges associated with the processing, purification, and production of simple, usable molecules from the decomposition of stable natural polymers. These challenges can be found in the fact that significant challenges are still associated with the processing, purification, and production of simple, usable molecules. This is the case even though it is considered an appealing approach to achieving sustainability goals. It is essential to subject AW to additional pre-treatment in physical, chemical, or biological treatment to derive the greatest possible value from this waste category.

Because of the potential for agro-industrial waste to be utilized in producing a wide variety of chemicals, animal feed, antibiotics, antioxidants, biofuels, enzymes, and vitamins, this fact must be brought to people's attention and thoroughly comprehended. In addition, it is essential to realize and accept this fact. Fermentation, which takes place while the substance is still solid, is the method that is used to produce all of these things (SSF). As a direct result, many distinct microorganisms are utilized to manufacture various valuable commodities. The primary origins of these goods can be traced back to agricultural processing businesses such as those that specialize in the production of malt, cereal grain milling, oil seed extraction, malt, and fruit and vegetable processing, as well as other enterprises that function analogously. When producing necessary commodities, manufacturers frequently make use of a wide array of distinct sorts of waste products that are produced as a byproduct of industrial processes. The following are some examples: wood and scrap wood, a variety of solvents and chemicals, waste, oil, weed grass, waste from a restaurant, soil and gravel, brick and concrete, and a variety of other materials of a similar sort.

On the other hand, the technologies used in agriculture produce many distinct kinds of materials grouped and referred to as AW. The following items are considered instances of this waste category: bedding, plant stalks, vegetable debris, hulls, and leaves. It is possible to use this AW, which is generally understood to be the byproduct of actions that take place in agricultural contexts in various ways, depending on the unique circumstances.

There is much industrial waste, but three types can be used for productive use. These types of waste are chemical, toxic, hazardous, and solid. This possibility exists for various other sorts of industrial waste as well. Processing facilities, distribution hubs, and manufacturing establishments generate the vast bulk of chemical waste. They are, moreover, accountable for most of the waste produced. The term “agricultural waste” can refer to many things, including but not limited to waste, broken boxes, oil filters, pallets, tires, waste, rubber, and plastic. Oil filters are another component that can frequently be found in AW. To give just two examples, other AW goods include grapevines and trees with fruit still on them. It is necessary to be conscious of and knowledgeable that agricultural residues have a very high concentration of bioactive chemicals. Being aware of and knowledgeable about this fact is essential. This must always be kept in mind and should not be forgotten. Mushrooms, biogas, biofuel, and raw materials for various other industries could all be produced using these wastes if utilized appropriately. All that is required is the proper application of these wastes. All that is required is that these wastes be used appropriately. When these things are employed, there is a corresponding reduction in the overall pollution caused to the surrounding area’s environment. In addition to the vitamins, enzymes, antioxidants, and other substances created during SSF, the wastes consist of items like animal feed, as mentioned earlier. Acetate, produced as a byproduct of fermentation, is one example of another type of waste (SSF). After that, the things that were given an added value are put through a procedure that entails in-depth analysis and debate for a considerable time.

As a direct outcome of this, it is a widely held idea that agricultural operations and industrial procedures each result in the development of their distinct types of waste, which supports this belief. Using the SSF method to transform these wastes into valuable chemicals, the pollution can be reduced when discharged into the surrounding environment because it is well established that antioxidants protect the human body from the free radicals that are known to cause diseases such as arthritis, dementia, asthma, anemia, aging process, ischemia, and a variety of other conditions a type of radical scavenger. This is because antioxidants protect the human body from the free radicals known to cause these diseases. Antioxidants defend the human body against free radicals, the known culprits in developing various diseases and ailments (Jaleel et al. 2010). Natural antioxidants have been demonstrated to contain hepatoprotective capabilities and antiviral, anti-inflammatory, anticancer, and antitumor characteristics. The fact that natural antioxidants are less harmful and have these properties were discovered through experimentation with various substrates and microorganisms, which proved that natural antioxidants are less hazardous and have these properties. The amounts of protein, phenolic chemicals, fiber, and antioxidant characteristics in these wastes have grown due to this transformation. The wastes have the potential to be repurposed in such a way that they may be put to use for a broad number of different applications, and this is something that can be done with them. One of the numerous potential benefits that this could bring about is this.

It is of utmost importance that the practice of using waste products from agricultural and industrial processes in producing a wide variety of chemicals, animal feed, antibiotics, antioxidants, biofuels, enzymes, and vitamins be brought to light and acknowledged. This is because it is of the utmost importance that this practice is utilized. The fermentation procedure must be carried out in the solid state, which is necessary to produce everything here (SSF). Because of this, producing these important commodities requires the participation of a very wide collection of bacteria. This is because bacteria are essential to the process. The overwhelming bulk of these items is acquired from various agricultural processing companies. The processing of fruits and vegetables, extraction of oilseeds, manufacture of malt, and milling of cereal grains are just a few examples of businesses that fall under this category. Using the various forms of waste products generated by industrial operations, it is feasible to manufacture many objects that can be put to productive use. Materials such as wood and scrap lumber, chemicals, waste, oil, weed grass, waste from a restaurant, soil and gravel, brick and concrete, and a wide variety of other materials are included in this category. A different type of waste is called AW, which stands for AW. This substance is created as a byproduct of a wide variety of agricultural activities, and its components include things like bedding, plant stalks, vegetable waste, hulls, and many leaves. Its name comes from the fact that it is used as a bedding material. Other items can be made by recycling AW. This AW, also known as a byproduct of agricultural activity, can be utilized in various ways that will prove beneficial, and these uses can be found in various places. The benefits derived from utilizing this AW can be found in various places.

Solid waste, toxic and hazardous waste, and chemical waste are the three types of industrial wastes that have the potential to be utilized productively. The following are examples of other types of waste found in industrial settings: The vast majority of waste chemicals are generated in commercial and industrial settings, which might include various establishments such as processing plants, distribution hubs, and storage facilities. Items such as shattered containers, oil filters, pallets, tires, waste, and other forms of plastic and rubber are considered “agricultural waste.” Broken containers are also included in the box. Grapevines and other types of plant material could be included in the category of AW. This category also includes other types of plant debris. This fact needs to be acknowledged and comprehended, as agricultural residues contain a very high and abundant number of bioactive compounds. This is a truth that needs to be recognized and understood. A significant amount of these chemicals can be found in agricultural leftovers. If these wastes were profitable, a wide variety of products, such as mushrooms, biogas, biofuel, and raw materials for several other enterprises, could be produced if they were put to productive use. When these things are utilized, there is a marked reduction in the overall quantity of pollutants discharged into the surrounding environment. As was said before, the wastes include animal feed, vitamins, enzymes, antioxidants, and other chemicals formed from SSF. In addition to this, the wastes also include a variety of other substances. All of these objects are categorized as chemical substances (SSF). After this, the components contributing to the total value are broken down into constituent parts and given a close analysis.

Thus, it is commonly established that industrial wastes and AWs are distinct categories. During the SSF process, these wastes are converted into compounds that reduce environmental contamination. Antioxidants are a form of radical scavenger, as it is known that they protect the body against free radicals that cause diseases such as arthritis, dementia, asthma, anemia, aging, ischemia, etc. Using different substrates and microorganisms show that natural antioxidants are safer and have hepatoprotective, antiviral, anti-inflammatory, anticancer, and antitumor properties. When these wastes are converted, their protein, phenolic, fiber content, and antioxidant qualities increase. The wastes can be treated to be utilized for various useful applications. Hence, agricultural and industrial byproducts may be effectively exploited by changing them into useful molecules. Agricultural and industrial wastes can be converted into valuable goods with the SSF process. Using microbes and various substrates, waste products can be converted into potentially beneficial compounds, such as antioxidants. In addition to reducing environmental contamination, this provides a sustainable source of valuable molecules. In addition, the transformation of waste into valuable molecules can increase the economic value of these resources and open up new avenues for the manufacturing of high-value goods.

17.10 Conclusions

AW, generated from activities such as farming, livestock rearing, and seafood farming, may contain helpful compounds and can be converted into beneficial resources through the “3R” management strategy: reduce, reuse, and recycle. This saves waste and provides new income prospects for farmers and processors. Waste production in agro-based enterprises is inevitable due to the nature of agricultural production, influenced by input substrates, procedures, and production size. Effective management of AW through the 3Rs can reduce negative effects on the environment and human health and provide opportunities for value-added products and biofuels. The amount of AW utilized should be defined by the type of agriculture and simultaneous operations, and engaging in the recovery, recycling, and reuse of AW can lead to valorization and protect the environment.

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Decentralized Composting and Vermicomposting for Agricultural Waste Management: Recycle at Source

18

Chaichi Devi and Meena Khwairakpam

Abstract

Agricultural wastes mostly comprise biodegradable waste unlike urban mixed wastes. Every stage in agricultural process generates wastes. Disposal without proper management creates many nuisances to the environment. Soil contamination, nearby water pollution, and air pollution are the results of burning of agricultural wastes or simply dumping in open land. Considering as resource, agricultural wastes may become raw material for various value-added productions. Compost preparation is one of them. Decentralized waste management facilities are where waste is handled by small units. Agricultural waste management by decentralized vermicomposting unit is helpful not only to scale up the management system but also to develop agribusiness for marginal local farmers. The biomass for a small area is processed in vermicompost unit and after value addition is sold by farmers for further applications. Recycle of raw materials at source, environment friendly technology, economic benefits are associated with decentralized composting and vermicomposting for biowastes. These green technologies are cost-effective and easy to install with zero emission. In the current chapter, all the aspects related to decentralized agricultural waste management is discussed.

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Keywords

Agricultural wastes · Decentralization · Composting · Vermicomposting · Recycle · Small-scale industries · Circular economy · Sustainable development

18.1 Introduction

The operations in various agricultural activities generate many of the unwanted materials. The nature of agricultural waste is mostly biodegradable. Biodegradable wastes are organic in origin and are degraded naturally by other organisms. Various abiotic and biotic factors are associated with the biodegradation process. Complex organic molecules are broken down into simple molecules that can be recycled back into the system unlike inorganic wastes. The decomposition process comprises either aerobic or anaerobic activities. Agricultural wastes can be categorized depending on their source: farm wastes during production, harvesting wastes, livestock wastes, run-off as wastewater, pruning, clearing of weeds, etc. The major benefit of agricultural wastes is the utilization in many ways. Agricultural waste management is the major boon for the economy of developing countries like India. Furthermore, agriculture is the occupation of majority of the population of such countries. The opportunities are huge if proper policies are developed by government initiatives. Biomass conversion into value-added product is the backbone of sustainable development (Prasad et al. 2020). A thorough analysis was done on agricultural wastes from 1931 to 2018. The utilization of agricultural wastes has been studied for more than 60 years worldwide. Scientific study has been more pronounced for the last 13 years. Agricultural residues are explored for utilization. Most of the researches are carried out in China. The last decade is devoted mainly on green economy. The advancement of technologies led to studies on biomass utilization to combat global energy requirement. Alternative sources of energy are in demand to mitigate climate change. Sustainable development goals set by the UN to be achieved within 2030 mainly focuses on green energy and food security (Duque-Acevedo et al. 2020).

Biodegradable wastes in rural area mostly comprise plant-based wastes, whereas the nature of biodegradable waste in urban area is different. Mostly in rural areas, the waste is homogeneous and not difficult to segregate. The major difficulties arise at the time of disposal. Inadequate handling of biowastes leads to environmental degradation in terms of various pollutions. The major by-products are toxic chemicals, harmful microbes, and heavy metals when is not properly disposed. The dumping of decomposable compounds without proper management results into an anaerobic condition. The release of methane gas is the major consequence of such situation. Methane is the major contributor to climate change. Proper management facilities are important to reduce methane emission from agricultural activities. On the other hand, when open burning is practiced, it releases another greenhouse carbon dioxide into the atmosphere. Therefore, a proper alternative approach for agricultural waste management is a must for sustainability (Popoola 2022). Based on the decomposition process, many of the technologies have been developed for bioconversion of biodegradable wastes. In recent times, advanced technologies have been able to handle large quantities of wastes.

18.2 Agricultural Wastes to Wealth

Waste cannot be defined by looking at the nature of the material. Anything discarded becomes waste, but it does not mean it has lost its value. The discarded wastes may become raw material for any valuable product development. Waste can be converted into wealth. The value addition of agricultural waste is large for economic gain. The traditional methods of disposal of waste must be avoided for better environment. The various technological advancements have already proven to be important alternatives for biowastes management in various industries. Agricultural biowastes in rural areas may lead to micro-entrepreneur development among the marginal farmers. Livelihood generation, upliftment of quality living, economic gain, and sustainable environment is possible by bringing back the waste into the loop. This is the major concept behind circular economy based on bioeconomy (David 2020).

Various options are available for the management of agricultural biowaste. Different biodegradable wastes are studied for the production of value-added products. The technologies are discussed in the following section. Waste to organic fertilizer is the most important management option looking into the United Nations Sustainable Development Goals 2030 (Eyhorn et al. 2019). Demand of food production rises with an increase in population. Food security is another issue to be addressed, as application of chemicals fertilizers leads to bioaccumulation of toxic in the food chain. Organic manure and organic farming are the most important concerns for sustainable development. Health of the future and current generations depends on the healthy production of foods. Soil health is another aspect apart from human health. Soil productivity is decreasing worldwide due to prolonged application of chemicals. The various revolutions in the past decades regarding farming activities had negatively impacted the society and environment. The green revolution in India started in the 1970s for agricultural productivity in large scale based on chemical fertilizers. Instead of being a boon, in the near future, it is proven to be a curse. Soil deuteriation, water contamination, and atmospheric pollution are the major harmful impacts of chemical applications in farming. On the other hand, the cost of chemicals put the marginal farmers into debt. The producers of the chemicals were the benefiter of the lion share. The green revolution in the past was important to combat malnutrition and overcome hunger of the deprived population. But the revolution was not actually green. The future green revolution depends on food security without compromising the environment (Phillips 2014). Food is not the only thing necessary; for a healthy life, an evergreen environment is required. Clean water, air, and soil are the major components of healthy environment. The natural resources must be conserved for the future generation for sustainable development. The farming activities must go back to the basics. Technologies must be developed without compromising environmental justice (Thompson 2009).

All these green technologies ultimately convert waste to cash. But the only difficulty arises when the technologies are practiced on ground. Handling of a large quantity of wastes and transportation facilities are few of the hindrances in their implementation. The major problem can be tackled when waste is processed at source. Installation of the abovementioned recycled options is not so difficult at source, although proper planning and policy are important for any facility. Decentralization is the option where small units are set up to handle small quantity of wastes in an efficient manner (Bruni et al. 2020). The advantages of decentralization are mentioned below:

- Minimizing burden on landfill sites. Difficulties in disposal can be overcome.
- Instead of handling large quantities of wastes, a small number of wastes is processed efficiently.
- Environmental pollution is reduced. Pollutants released into the water, atmosphere, and soil are checked.
- Opportunities for waste to wealth is realized with the benefits of local communities. Community of a particular area is directly involved in handling their own resources. They are educated and trained in technology for the establishment of small enterprises.
- Waste is recycled at source, and transportation cost is reduced.

18.3 Composting Technology

Composting is a biotechnological process of degradation of organic matter with the help of microorganisms in the presence of oxygen (Fig. 18.1). Vermicomposting is an advanced form of composting technology in which earthworms are used along with microorganisms in decaying process.

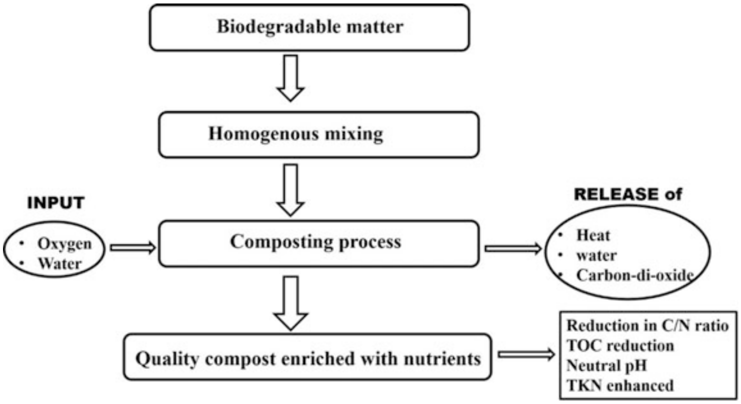

Fig. 18.1 Mechanism of composting technology

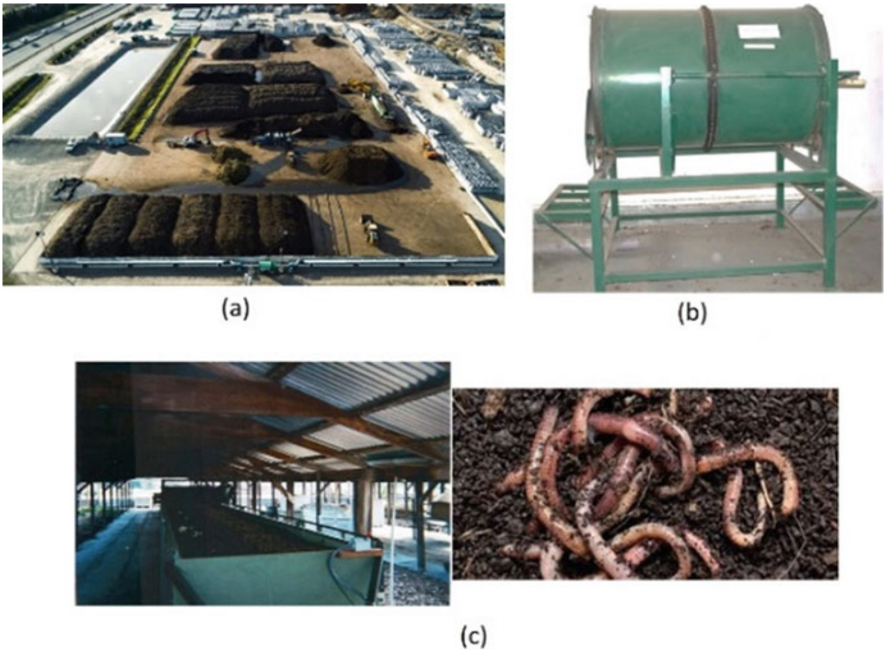

Fig. 18.2 (**a**) Open composting (https://www.compostingtechnology.com/aerated-static-pile-systems/). (**b**) Closed or in-vessel composting (Varma and Kalamdhad 2016). (**c**) Vermicomposting (https://www.o2compost.com/vermicomposting.aspx)

Composting can be classified according to the device used for oxygen supply: open composting and closed composting (Bernal et al. 2017; Lin et al. 2019) (Fig. 18.2). In open composting the biomass is exposed directly to the air for oxygen supply. The types of open composting are as follows:

- Static pile: In this process the biomass remains static. Oxygen is supplied through air pipes under the material with some pores in it. Nuisance like odor can be overcome by collecting exhaled air with biofilter.
- Windrow composting: This is another type of open composting. The reactors are constructed in rows without covers, and agitation is done through frequent turning as well as rotating of the biomass. It is an active composting process lasting for around 8 to 16 weeks. The favorable conditions are required to maintain for a successful result. Natural aeration is proved to be more successful than mechanical aeration (Gopikumar et al. 2020).

The closed system is also termed as in-vessel system. One of the popular in-vessel composting is rotary drum. Rotary drum has a capacity of 550 L and is ideal to be set up on a field. The metal handle is used for rotation, and the base of the drum is metallic. The size of the sheet used for drum construction is around 4 mm. The added advantage of drum composting over open composting is the aerobic condition where various useful microflora flourish for the active degradation process. Proper mixing results into shorter duration to complete the process. The final compost is more stabilized (Varma and Kalamdhad 2016). The turning frequency of the drum for agitation affects some of the parameters such as pH, Electical conductivity (EC), Total Kjeldahl Nitrogen (TKN), Total Organic Carbon (TOC), and the final compost to be prepared. A turning frequency of once a day helps in maintaining the thermophilic phase for the required period to achieve optimum results (Kalamdhad and Kazmi 2009).

The total environment is very important for composting. The major parameters that influence the composting process are moisture, aeration, and temperature. Moisture must be maintained between 45% and 50%. Depending on the nature of the composting process, the moisture requirement may vary. In vermicomposting around 70% of moisture is ideal for earthworm metabolism. The temperature must be optimum for humification, aeration, evaporation, and degradation. A very humid climate may lead to leachate problem. On the other hand, low temperature slows the degradation process by affecting microbe metabolism. Proper oxygen supply is a must to maintain aerobic condition. The degradation process remains incomplete if anaerobic condition arises. Apart from these, few chemical and physical parameters are important. The C/N ratio of the substrate is highly associated with the degradation process. Various substrates have different carbon contents. The role of bulking agents is important to maintain the balance. A higher C/N ratio in the final product may lead to nitrogen starvation in the soil. Incomplete composting leads to phytotoxicity. Stabilization must be monitored before the applications. pH is also an important factor during composting. A pH between 5 and 8 is favorable for microorganisms. The interim mineralization may increase the pH during the process and mostly depends on the raw material. Neutral pH signifies maturation for soil application of compost (Azim et al. 2017). The bulk density and porosity of compost are important. Porosity of the compacted material ensures proper oxygen flow. The particles must be broken down into regular pieces before feeding into the reactor. Otherwise, large particles will block the pores and oxygen supply. On the other hand, the bulk density of the final product is important for transportation (Azim et al. 2017; Jain et al. 2018).

18.4 Decentralized Composting and Vermicomposting

Aerobic degradation of organic waste is termed as composting. Compost is considered as an organic fertilizer. Compost application is important to balance nutrient cycle. Soil health is improved in comparison with chemical fertilizers. Continuous recycling is possible where the discarded biomass is put back to the system. This is referred to as circular economy based on bioeconomy. Every resource is valuable, and value addition through proper technology is important to reduce waste disposal in a community (David 2020). Vermicomposting is an advanced biotechnological process of composting in which earthworms are used in the bioconversion process. Vermicomposting is a lengthier process than composting, but the quality of its final

Table 18.1 Different biowaste bioconversion through composting and vermicomposting

Biowaste	Reference	Compost characteristics
Agricultural waste	Prasad et al. (2020) and Raza et al. (2022)	C/N ratio: 10–20 NPK: 19%, 38%, 61%
Weed biomass	Dissanayaka et al. (2023) and Devi and Khwairakpam (2023)	C/N ratio: <20 TKN: 2.93% TP: 11.03 kg^{-1} TOC: 24.03%
Vegetable waste	Varma and Kalamdhad (2016)	CO_2 evolution reduction: 88% Increase in K: 33% TOC reduction: 15.4% pH: 6.5–8
Paper mill sludge	Wang et al. (2021)	Humic substances: 44.42 mg g^{-1}
Municipal biowaste	Angeriz-Campoy et al. (2023)	pH: 7.8
Coconut husk	Swarnam et al. (2016)	NPK: 1.6:2.4:1.3 C/N ratio: 15–20
Palm industry waste	Rupani et al. (2017)	C/N ratio: 17.2 N: 1.76
Distillery industry sludge	Suthar and Singh (2008)	TOC reduction: 27.2%
Floral wastes	Etheredge and Waliczek (2022)	pH: 7 C/N ratio: 21.6

product is superior than that of the traditional compost. Earthworm metabolic activities enable more nutrient recovery in the final vermicompost (Devi and Khwairakpam 2020a, b). Bioconversion of various biowastes is studied in recent time (Table 18.1). The combination of both technologies helps reduce the time required to obtain stable products. Many of the biowastes are examined for the combination of composting and vermicomposting. It was observed that the quality of the value-added product is obtained within a shorter period (Varma and Kalamdhad 2016; Devi and Khwairakpam 2023). Various agricultural wastes are investigated for bioconversion, and research is ongoing for the evaluation of different farm wastes bioconversion through composting and vermicomposting. Successful results are obtained for harvest wastes, livestock wastes, weed biomass, etc. (Devi and Khwairakpam 2020a, b, 2023; Bouhia et al. 2023; Barus et al. 2023; Hidalgo and Corona 2023).

The final compost and vermicompost from various biowastes are proven to be rich in nutrients (Devi and Khwairakpam 2020a, b; Barus et al. 2023). The soil quality was improved after application and was restored. The major criteria for any compost is to meet the standard quality before practical applications. The standards are more or less similar in all the countries with a slight variation depending on their soil requirement. Compost quality parameters are listed in Table 18.2 according to the US composting council.

Table 18.2 Compost and vermicompost characteristics according to the US composting council

Parameter	Standard quality
C/N ratio	≤20
Organic matter	≥25%
pH	6–7
EC	≤4 ds/m
Particle size	≥95% passing through a 16-mm screen
Color	Dark brown
Odor	Earthy
Moisture	40%–60%

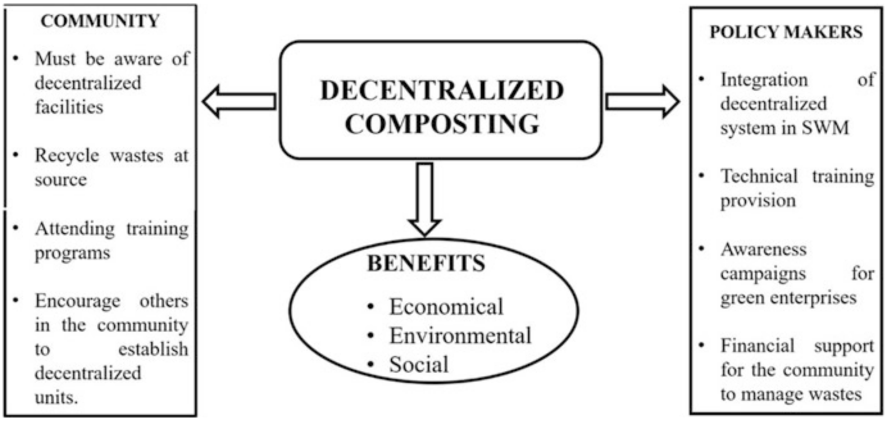

Fig. 18.3 Decentralized composting (based on a case study in Chicago in an urban area) (Pai et al. 2019)

Establishment of small-scale composting facilities in a local area is called decentalized composting unit. The waste is not transported to large facilities or landfill sites. The burden on the management is reduced to a large extent. A decentralized composting facility is not only beneficial for waste management but is also economical and sustainable (Fig. 18.3). The major advantage is the minimal capital cost for infrastructure, employment generation, and affordability. On farm composting, facilities are in trend in recent times and practiced in various countries. Successful models are examined, and developing nations are encouraged to adopt the same (Bruni et al. 2020). A comparative study of centralized and decentralized composting was conducted.

It was observed from spatial analysis that there is cost-cutting in the decentralized system. The major benefits of decentralization are recycling at source, resource recovery through circular economy, and reduction in greenhouse gas emissions. Carbon footprint is also significantly reduced as the centralized system is mostly energy-driven. Green technologies, anaerobic digestion for urban waste, and decentralized composting in rural areas are the most promising climate-friendly options for biowaste management (Weidner et al. 2020). Many successful decentralized facilities are documented in various case studies around the world. The major challenge is the landscape and characteristics of wastes. The total economic turnover was $100/Mg from a case study in decentralized city composting in Chicago. The major economic advantage was observed in cost-cutting for landfilling. The portion of budget allocation for sanitation and transportation of disposal of waste was nearly 10%. On the other hand, selling of compost to community parks and other facilities involves a huge saving of the city government in Chicago (Pai et al. 2019).

Biowaste management is a major concern as the accumulation is increasing day by day with the increase in population. Bioeconomy is the modern way for sustainable future. The European Union (EU) has established the European Composting Network bringing policy makers, biowaste managers, consultants, researchers, under the same umbrella. The compost recovery from organic materials on an average 5.2% annually since 1995. The return was 116 million tons in 2017. These policies are widely adopted for urban biowaste management. Composting is the most demanded biowaste management in spite of being a conventional method. The legislations all over EU highly encourage decentralized composting, and many of the replicas for community biowaste management are implemented in different nations (Bruni et al. 2020).

The major benefits of decentralized composting and vermicomposting involve many aspects. The developing countries must adopt the policies to implement decentralized facilities for waste management without delay. The economically sustainable process as it reduces major cost of transportation of wastes to disposal facilities enabling treatment at source. The finished produced is utilized locally without involving any retailer. Community natural areas, gardens, and institutional premises are the top buyers. Local government as well as local community is benefitted with a major share. Source separation, natural resource utilization, and energy saving in chemical fertilizer manufacture are few of the ecological benefits involved in decentralized composting. On the one hand, social benefits involve small enterprises established with limited training, cost-saving in chemical purchase, and low cost involved in composting unit installment (Pai et al. 2019). If we consider globally, decentralized composting is a promising tool to fulfill policies related to resource conservation and climate change through solid waste management. The nutrients are returned to soil without any environmental depletion, with benefits to marginal farmers, and the community makes decentralized composting a new trend for the treatment of all kinds of organic wastes. Already developed countries have realized the connection between resource flow and waste recycling to close the loop. The lack of awareness and other factors are the hindrances to the low rate of decentralized composting in developing countries (de Souza and Drumond 2022).

The requirements for decentralized composting are as follows (Bhave and Kulkarni 2019):

- The availability of biowaste in adequate quantity.
- Segregation of waste at source and recycle at source. Rural areas do not face difficulty as the waste is mostly homogeneous.

- Selection of proper composting method based on local environmental conditions and nature of the raw material.
- Engagement of local community for a successful implementation.

18.5 Major Challenges in Field Implementation

The challenges are involved in decentralized composting. The major challenges for planners to adopt existing models are the diversity in topography and demography. Waste characteristics vary according to geographical and societal disparities that lead to difficulties for planners to set up any facility. Finding a suitable location is another challenge. There are many factors to be considered before composting. Environmental factors, availability of raw materials, topography, and social factors like nuisance to neighborhood are the key points to be considered before selecting sites. The ideal locations are community parks, institutional premises, office premises, etc., in urban as well as rural areas (Pai et al. 2019). In the case of agricultural wastes, the onsite composting facilities in the farmer's field is an ideal and added advantage. The major challenge involved in agricultural waste decentralized composting is the characterization of raw materials. The quantity is important for a maximum return. If the quantity is high, collection of raw material involves labor cost and storage cost before composting. The environment is another factor. The environmental factors highly influence the composting process depending on the raw material (Devi and Khwairakpam 2020a, b). Moisture content and organic carbon are the major characteristics of the feed of compost, which is dependent on temperature and humidity for a successful decomposition. These are few of the challenges in field implementation, unlike laboratory setup.

18.6 Agribusiness

The major advantage of on-farm composting is the availability of raw material at source. Biomass generation from various farm activities are the added advantage to establish decentralized composting in rural areas. Agriculture may become a two-way process. One way is the production of agricultural products and another is the organic manure production from agro-wastes for soil application in farmlands. Agribusiness is the major milestone for circular economy. It is defined as economic venture connected to agricultural products. Biowaste generated in farms are the by-products that can turn into valuable resources when managed properly. Many of the agricultural residues are proven to be important raw materials for composting. Biomass always requires proper treatment before discarding. Composting is the ideal technology with added advantages for biowaste management. The practical applicability is examined in various studies. Pilot-scale composting for agricultural wastes met the standard of the Chinese National Agricultural Organic Fertilizer when the final compost quality was assessed. Bioconversion of agricultural waste mix is possible in pilot-scale composting (Bian et al. 2019). Cost-benefit analysis of decentralized composting business was done in a Nairobi model. Economic and environmental benefits are high in percentage. The major environmental impact is on the reduction of greenhouse gas emissions by sequestering 1.21 tons of carbon dioxide through composting. On the other hand, economic profit is 70% with the successful implementation of decentralized composting unit. Cost-effectiveness and economic feasibility make decentralized composting an important technology for agricultural waste management in rural areas. Small-scale industrial development with huge employment generation is possible along with other agricultural activities (Gebrezgabher et al. 2021).

Organic farming balances the ecosystem. Inputs are natural in the application of organic fertilizers contrary to adversity caused by outside agents in chemical fertilizer applications. The combination of traditional values, advanced scientific studies, and technology is a sustainable approach. Organic fertilizers are produced through the bioconversion process. Organic inputs are globally uniform due to the effort of the International Federation of Organic Agriculture Movements. The goal of the movement is to maintain soil health, ecosystem, and the healthy life of the people (Thompson 2009).

18.7 Conclusion

Decentralized organic waste management comprises economic, environmental, and social benefits. Cost-benefit involves biowaste recycling at source, low capital investment for setup, employment, and small-scale industry development, which are beneficial for marginal farmers and soil health maintenance. Socially acceptable technology as it is easy to handle, there is zero emission, involvement of local people in handling their own resources, high economic return. These technologies are a solution to the global issue of climate change. The phrase “think globally and act locally” is appropriate for decentraized composting facilities and realized when practically applied on ground. Decentralization helps reduce energy consumption and greenhouse gas emissions in various activities involved in large quantity of organic waste management in a central facility. Sustainable development goals particularly food security and zero hunger can be achieved through recycling of agricultural byproducts to produce organic manure. Organic farming is the only solution for sustainable development to secure healthy environment for the future generation. On the other hand, optimal use of natural resources is important for circular economy. This is only feasible when considering waste as wealth. Economy based on biowastes has many dimensions for the wealth of a nation and livelihood security of the people.

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