CHAPTER 1

FUNDAMENTALS OF BIOMASS WASTE VALORIZATION

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Abstract

The devastating impact of climate change and the necessity for sustainable products and processing approaches are significant concerns for the worldwide population. Interestingly, there is an abundance of biomass resources, which might meet the increasing demand for green products, as using fossil fuels is no longer recommended due to environmental concerns and sustainability. Biomass resources (renewable feedstock for renewable energy generation and specialty chemicals) are sourced from several natural sources and have a variety of applications. Most developed economies follow linear consumption concepts that are not feasible in the long term. The circular bioeconomy concept is a promising solution to minimize waste landfilling, generate revenue, and maximize zero-waste by utilizing biomass waste. The valorization of cellulose, lignin, and hemicellulose fractions into bioproducts, biofuels, or specialty chemicals depends on the practicality of their pre-treatment and further processing approaches. This chapter discusses biomass feedstock history, valorization processes, and applications, and motivations for their exploration. Several value-added products, which can be harnessed from biomass and residues, are detailed.

Keywords: Zero-waste biorefinery, Biomass waste, Circular bioeconomy, Value-added products.

1.1 Introduction

The considerable rapid increase in the world's population and industrial production has resulted in prevalent disorder, including the impacts of climate change. The increased usage of fossil-based resources has worsened these disputes (Rahimi *et al.* 2022). The disposal, usage, and management of biomass waste is a growing problem for urban areas, particularly in developing nations, because of the output of biomass waste and a shortage of practical techniques for recovering these waste resources (Zhou and Wang 2020).

Most developed economies are based on linear consumption concepts. These models, sometimes known as "throw-away" or "take-make-dispose" models, are not feasible in the long-term (Khoaele, Gbadeyan, Chunilall, *et al.* 2023). At this moment, the environmental, economic, and societal consequences necessitate immediate action. In the circular bioeconomy concept, resources are utilized as much as possible, the highest value is extracted, and products are recovered and regenerated at the end of their lifespan (Jõgi and Bhat 2020; Khoaele, Gbadeyan, Chunilall, *et al.* 2023).

Circular bioeconomy is a zero-waste biorefinery that promotes green and economical waste disposal. Furthermore, bio-based industries have environmentally beneficial attributes such as non-toxicity, biodegradability, and biocompatibility, encouraging an eco-friendly trend. Bioprocesses that convert waste into value-added biofuels and biomaterials can significantly minimize reliance on fossil resources as feedstocks, preventing natural resource depletion. Biomass waste has been valorized into environmentally acceptable bioproducts such as medications, specialty chemicals, cosmetics, biofuels, biopolymers, and animal feed (Cheirsilp and Maneechote 2022; Romaní *et al.* 2020**).** The valorization of lignocellulose biomass into value-added bioproducts is an alternative to fossil resources as raw materials. This strategy aims to preserve the energy environment, mitigating greenhouse gas emissions such as carbon dioxide from burning fossil energy sources and minimizing carbon footprints (Dessie *et al.* 2023).

Conventional lignocellulosic biomass (LCB) is abundant in agro-industrial, forestry, and agricultural industries. Their examples are tree bark, sawdust, leaves, brewers spent grains, sugarcane bagasse, peels, shells, and husks such as wheat, sorghum, barley, rice, corn, oil palm stalks, straw, sunflower stems, switch grass, black liquor, waste papers, cotton residue, pomace, etc. (Ab Rasid *et al.* 2021). LCB consists of cellulose, lignin, and hemicelluloses, which exist in different quantities. Celluloses, the most abundant biopolymer, and renewable carbon substitutes, are linear homopolysaccharides of glucose linked by b-1, 4-glycosidic bonds. Hemicelluloses are a group of heteropolysaccharides made of b-1, 4 connected backbones of five sugars: L-arabinose, D-xylose (C5), D-glucose, D-galactose and D-mannose (C6) [9], [10]. Biomass feedstock can be recovered from nature as waste and can be categorized as follows in Figure 1.1 and Table 1.1.

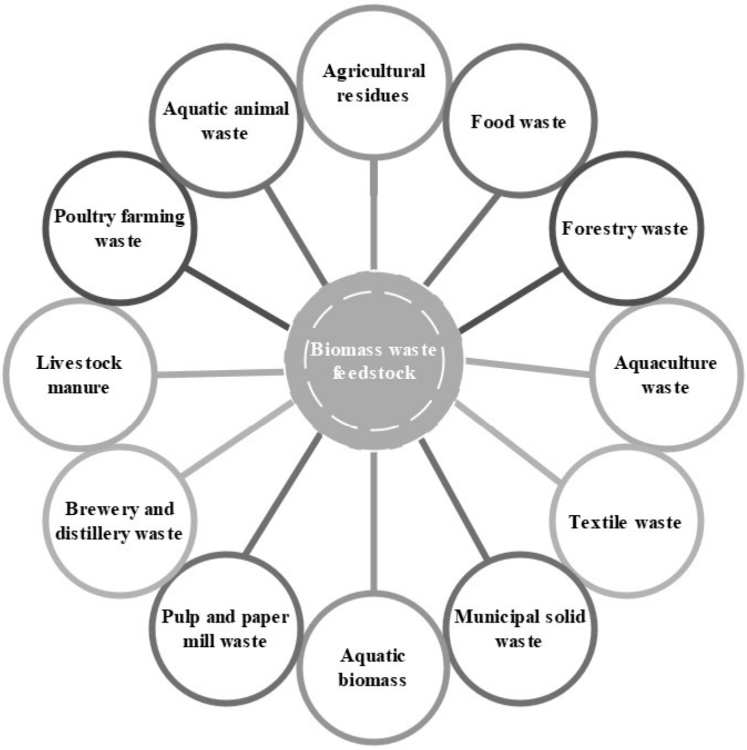

Figure 1.1 Waste feedstock for zero-waste biorefinery (Maroneze *et al.* 2022).

Table 1.1 Biomass waste feedstock from various industries and their potential high-value products (Khoaele, Gbadeyan, Chunilalla *et al.* 2023; Gbadeyan *et al.* 2022; Tesfaye *et al.* 2017; Daroch, Geng and Wang 2013; Maragkaki *et al.* 2018; U. Lee *et al.* 2023).

Waste Feedstock	Biomass Type	Biomass Waste Resource
Agricultural Residues	Crop Residues	Non-edible components of crops such as rice, wheat, and corn are frequently abandoned in fields or burnt, generating greenhouse gases. These leftovers might generate bioenergy, make bio-based goods, or serve as fuel for biochemical processing.
	Straw	Straw from grains such as rice, wheat, and barley is widely regarded as agricultural waste. It may, however, be utilized for bioenergy, animal bedding, and mushroom growing as a substrate.
Food Processing Waste	Pomace	Fruit and vegetable pomace is produced during the juice and oil extraction operations and consists of skins, seeds, and pulp. These by-products can be exploited to create dietary fiber, antioxidants, and bioactive substances.
	Grape Marc	Winemaking waste like grape skins, stems, and seeds may be converted into high-value products such as bio-based chemicals, cosmetics, and dietary supplements.
Forestry Waste	Forest Residues	Branches, leaves, and other wooden residue are frequently left on-site or burnt during logging and forestry activities. These wastes might be utilized to produce bioenergy, charcoal, or bio-based compounds.
	Sawdust and Wood Shavings	Wood processing by-products are occasionally underused. They can be converted into heating pellets, animal bedding, or raw materials for bio-based products like biocomposites.

Aquaculture Waste	Aquatic Plant Waste	Water hyacinth or duckweed, which proliferate, can be utilized to generate bioenergy, feed animals, or recover nutrients.
Textile Industry Waste	Cotton Residues	Cotton stalks, seeds, and husks are frequently thrown away in cotton production since they are not used for textiles. These wastes might be utilized to produce bioenergy, biomaterials, or oil.
Municipal Solid Waste	Organic Waste	Organic waste from households and industries, such as food leftovers and yard debris, is frequently dumped in landfills. Biogas, compost, and bio-based goods might be produced by implementing effective organic waste sorting and conversion processes.
Aquatic Biomass	Algae	Algae may be utilized to produce biofuel, treat wastewater, and extract vital nutrients such as omega-3 fatty acids.
Pulp and Paper Mill Waste	Black Liquor	A by-product of the paper manufacturing process, black liquor, contains lignin. It may be used as an adsorbent for wastewater treatment, as an adhesive, and for energy generation through processes like black liquor gasification.
Brewery and Distillery Waste	Spent Grains	Grains such as barley and maize are discarded after brewing or distillation. These discarded grains can be utilized as animal feed, as a source of bioactive chemicals, or as a source of bioenergy.
Livestock Manure	Animal Manure	Animal manure may be converted into biogas and biofertilizers by anaerobic digestion, minimizing methane emissions.

Poultry Farming Waste	Feather Meal	Feathers, a by-product of poultry processing, generate feather meal, a protein-rich animal feed ingredient aiding nutrient recovery. Amino acids, keratin, and other proteins can be extracted for utilization in the cosmetics, pharmaceutical, and textile industries.
Aquatic Animal Waste	Shell Waste Utilization	Shellfish shells like oyster and mussel shells can be used for soil amendment and wastewater treatment. They can also trap carbon when used as shellfish cultivation substrates. Snail shells can be used as fillers to strengthen biocomposites.
	Collagen and Gelatin	Collagen isolated from aquatic animal waste can be utilized in the cosmetic, pharmaceutical, and food industries. Gelatin, a protein derived from aquatic waste, is utilized in confectionery and food products.
	Fish Processing Byproducts	Fish processing produces waste materials like heads, tails, and viscera, which can be processed for fish food and oil.
	Phosphorus Extraction	Aquatic animal waste can be a valued resource of phosphorus, an essential nutrient for plant growth. Phosphorus can generate nutrient-rich fertilizers.

1.2 History of Biomass

Biomass has long been used as a source of fuel, building materials, and food. Humans have depended on numerous types of biomasses for survival and development throughout history. An overview of the development of biomass use is depicted in Figure 1.2 below:

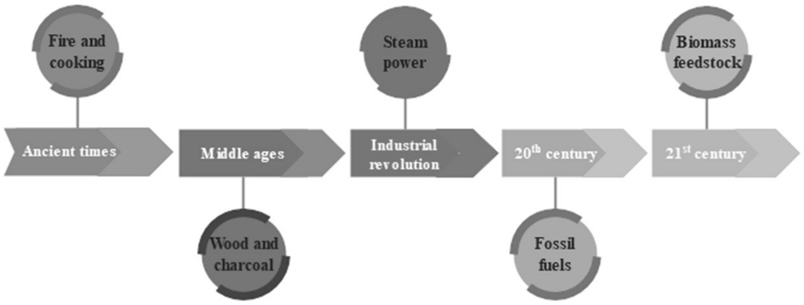

Figure 1.2 Development of biomass use over time.

1.2.1 Ancient Times

Fire and Cooking: Ancient people learned how to burn biomass, such as wood and plant materials, to generate heat and light. The ability to cook food, generate heat, and fend off predators was all made possible by this discovery. Most dry plant materials incinerate in the atmosphere at 220-300 °C or higher temperatures, emitting distinctive bioenergy in light and heat. At first, wood is exothermically pyrolyzed at roughly 260 °C to produce gaseous fumes and solid char. The char eventually turns to ash, and the smog eventually ignites. Fire, which is the combustion of organic matter, is essentially the rapid oxidation of bio-carbon molecules by oxygen at high temperatures and is depicted by Equation 1 as follows (Guo, Song and Buhain 2015):

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O + \text{heat} + \text{light} \qquad (1)$$

1.2.2 Middle Ages and Renaissance

Wood and Charcoal: For heating, cooking, and industrial processes, wood remained the dominant source of energy throughout the Middle Ages. Wood was partially burned to make charcoal, used to make fire in forges and for melting metal. High-grade charcoal is emitted by heating timber in a retort or kiln at roughly 400 °C without air until there are no volatiles (Antal and Grønli 2003). The pyrolysis reaction is depicted by Equation 2 as follows:

$$C_6H_{10}O_5 \rightarrow 3.75CH_{0.60}O_{0.13} + 2.88H_2O + 0.5CO_2 + 0.25CO + C_{1.5}H_{1.25}O_{0.38} \qquad (2)$$

Where $3.75CH_{0.60}O_{0.13}$ is charcoal and $C_{1.5}H_{1.25}O_{0.38}$ is tar.

Early Biochemical Processes: During this time, the concept of fermentation for brewing and food preservation evolved, providing the groundwork for later discoveries in biotechnology and biochemical processes. Microbes in traditional fermented foods change raw food components, enhancing their nutrition, longevity, and organoleptic and health promoting properties (Xing *et al.* 2023).

1.2.3 Industrial Revolution

Steam Power: The Industrial Revolution of the nineteenth century brought an industry shift toward mechanized, steam-powered industries. Biomass was used to create steam for power manufacturing plants, mills, and transport systems. Examples of biomass include wood and agricultural waste (Griffin, Hammond and Norman 2018).

1.2.4 20th Century

Rise of Fossil Fuels: The 20th century saw the discovery and widespread usage of fossil fuels (coal, oil, and natural gas), significantly reducing the need for biomass as an energy source. Fossil fuels have greater energy capacity and are easier to use and transport. Fossil fuels provide >80% of the world's energy demands and are today's primary energy sources. However, fossil fuels are non-renewable and have finite reserves (Guo, Song and Buhain 2015).

1.2.5 21st Century

Biomass for Energy: In the 21st century, there has been increased focus on biomass processing as a renewable energy source. To minimize greenhouse gas emissions and diversify energy sources, biomass power plants, biofuel production, and biomass co-firing in existing power plants have been increasingly used, as seen in Figure 1.3 (Corrêa, Campani and Furlong 2022).

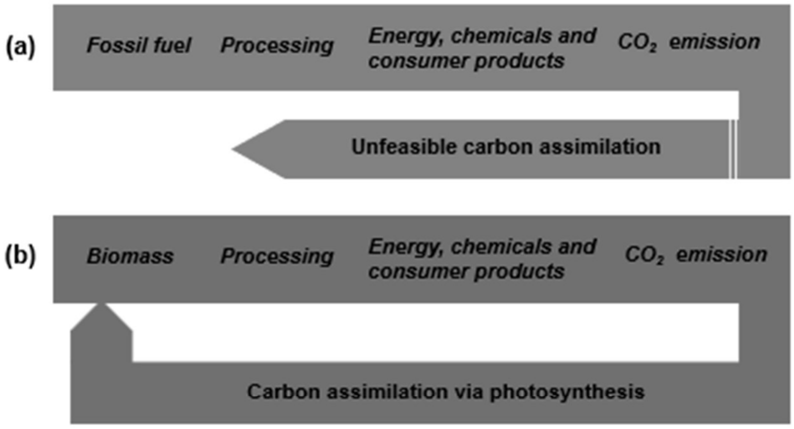

Figure 1.3 Processing cycles of (a) fossil fuel and (b) biomass (Corrêa, Campani and Furlong 2022).

1.3 Factors Leading to Biomass Valorization

The valorization of biomass waste into value-added products and energy evolved in response to several interconnected reasons. These elements highlight the importance of sustainable resource management, energy diversification, and environmental conservation. Several important factors have contributed to the development and implementation of biomass valorization protocols and are as follows:

1.3.1 Environmental Concerns

Sustainable and eco-friendly methods are becoming increasingly popular as people become more aware of environmental crises, climate change, air and water pollution, and the shortage of non-renewable resources. By removing organic waste from landfills and reducing greenhouse gas emissions, biomass valorization aids in protecting the environment (Kumar Sarangi *et al.* 2023).

1.3.2 Resource Scarcity

The demand for alternative renewable energy sources has been prompted by the limited availability of fossil fuels and the problems connected with their extraction, transportation, and combustion. As a widely accessible and renewable resource, biomass offers an attractive way of diversifying the energy mix and lessen reliance on fossil fuels (Kalair *et al.* 2021).

1.3.3 Circular Bioeconomy Concepts and Sustainability

The circular bioeconomy paradigm strongly emphasizes maximizing resource consumption, reducing waste generation, and shutting resource gaps. By converting waste materials into valuable goods, biomass waste valorization fits well with these tenets and helps to create a more sustainable and circular bioeconomic system. Ideas, including the circular bioeconomy and sustainability, have underlined the significance of biomass waste valorization. These concepts align with finding methods to turn organic waste, food waste, and other natural products into value-added products (Khoaele, Gbadeyan and Chunilall, *et al.* 2023; Ranjbari *et al.* 2022).

1.3.4 Energy Security

As the world's energy demand increases, a secure and diverse energy source is more crucial than ever. Biomass may be transformed into various energy sources, including biofuels and biogas, adding another energy source to replace conventional fossil fuels (Popp *et al.* 2014).

1.3.5 Policy and Regulations

Promoting renewable energy sources, reducing waste, and mitigating environmental effects are the goals of governments’ and global organizations' policies and regulations. The advancement of biomass valorization processes has been accelerated by incentives, subsidies, and regulations to produce bioenergy and the reduction of waste (Aliyu, Modu and Tan 2018).

1.3.6 Technological Advancements

Biotechnology, chemical, and engineering advancements have made the conversion of biomass waste into value-added products increasingly practical and cost-effective. These technical advances have created new opportunities for biomass usage and waste-to-energy operations (Varjani *et al.* 2021).

1.3.7 Economic Opportunities

The valorization of biomass has the potential to navigate new business possibilities and create employment in industries including waste management, manufacturing, and energy. Using biomass waste to create biofuels, biobased products, and specialty chemicals can boost local and regional economies (Babu *et al.* 2022).

1.3.8 Public Awareness and Consumer Demand

Consumer demand for sustainable goods and activities has increased due to rising environmental awareness. In response, businesses and industries are looking at how to use bio-based and environmentally friendly components in their goods, which can be made from biomass waste (Testa *et al.* 2016).

1.3.9 Research and Innovation

Developing new conversion techniques, enhanced catalysts, and improved strategies for effectively utilizing biomass waste have all been made possible by ongoing research and innovation in biorefinery. This ongoing learning has increased the potential for valorizing various biomass feedstocks. The spectrum of applications for biomass is being expanded because of ongoing research into effective biomass conversion processes like pyrolysis, torrefaction, and algae cultivation (Awasthi *et al.* 2020).

1.3.10 Waste Management Challenges

The increasing difficulty in handling organic waste streams, such as agricultural and food waste, has motivated the investigation of unconventional disposal methods for potential solutions. A sustainable and effective technique to handle these waste streams is through biomass valorization (X. Wang *et al.* 2022).

1.4 Biomass Waste Valorization Processes

The process of transforming biomass waste into value-added products is called biomass waste valorization. This approach is consistent with sustainable resource management principles, circular bioeconomy, and environmental impact reduction. Various process technologies can be used to transform biomass feedstock into marketable products. This classification approach identifies five main processes:

1.4.1 Collection and Sorting

Agricultural areas, woodlands, food processing plants, and industrial sites are just a few places where biomass waste can be found. Sorting is necessary to separate various waste types and eliminate pollutants (Zhou and Wang 2020).

1.4.2 Pre-Treatment

Pre-treatment is necessary for biomass waste to enhance its suitability for future conversion (Ab Rasid *et al.* 2021). Physical, physicochemical, chemical, or biological processes can all be used as pre-treatment procedures. Physical pre-treatment targets reduce particle sizes through grinding, milling, or chipping (Ramos, Monteiro and Rouboa 2022). To separate the microfibers of biomass, physicochemical pre-treatment uses a mixture of chemical treatment and physical shear forces, such as hot water, steam explosion, and ammonia fiber explosion. Chemical pre-treatment processes break down specific bonds within the biomass complex using chemicals such as acids, bases, and oxidizers (Bikash Kumar *et al.* 2020; Zhao, Zhang and Liu 2012). Biological pre-treatment processes utilize microbes and enzymes, such as alcoholic fermentation, anaerobic digestion, and photobiological (S. Y. Lee *et al.* 2019).

1.4.3 Biomass Conversion Approaches

Biomass waste conversion can be achieved using different processes, each fitted to its intended end-product, as illustrated in Figure 1.4. These methods include:

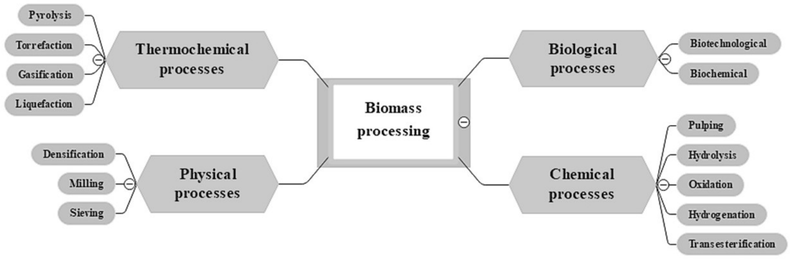

Figure 1.4 Processing techniques for biomass waste valorization into value-added products (Maroneze *et al.* 2022).

1.4.4 Thermochemical Processes

Thermochemical processes target the calorific value of the biomass and involve processes like pyrolysis, gasification, liquefaction, and torrefaction, as presented in Table 1.2 (Ghislain *et al.* 2020).

Table 1.2 Thermochemical processes for biomass waste conversion into value-added products.

Thermochemical Processes	Feedstocks	Temperature	Products
Pyrolysis	Cellulose, lignin, and hemicellulose	500 °C	Bio-oil, charcoal, and gaseous fuels
Torrefaction		200-350 °C	
Gasification	Flammable gas mixture	800 °C	Syngas
Liquefaction and algae	Agro-residues	150-420 °C	Char, biofuels, fertilizers

Pyrolysis converts wood waste into bio-oil, charcoal, and gaseous fuels through fast pyrolysis, usually without oxygen at 500°C. Gasification converts flammable gas mixture through partial oxidation at an elevated temperature of roughly 800°C into syngas, which is further used to produce methanol. Liquefaction varies from the previous two processes. Liquefaction converts biomass into liquid fuels at lower temperatures between 150-420 °C and higher pressures between 1-240 bars (Brajesh Kumar *et al.* 2022). Torrefaction is also mild pyrolysis due to its similar processing. However, it occurs in the absence of oxygen or at low concentrations, and at lower temperatures between 200-350 °C (Jeguirim and Khiari 2022).

1.4.5 Biological Processes

While thermochemical processes focus on converting heterogeneous substrates into a homogenous intermediary, biological processes often target the complex makeup of lignocellulosic feedstock. Consequently, while specific conversion occurs, there is an interest in preserving the monomeric or oligomeric makeup of the macromolecules included (Ghislain *et al.* 2020).

1.4.6 Biotechnological Processes

Biological approaches promise to use biomass waste or low-value materials to generate energy and construct a waste-to-energy interconnection. Dark and photo-fermentation are the most often utilized biological processes to manufacture bio-hydrogen from waste as organic substrates. The biological synthesis of hydrogen from biomass waste is a viable option (Sharma *et al.* 2020). Microbial and enzymatic processes can convert biomass waste into enzymes, bio-based chemicals, and bioplastics (María Diaz-Montaño 2020).

1.4.7 Biochemical Processes

Biochemical processes convert feedstock into end-goods in one or two steps under mild reaction conditions (mild pressure and temperature). This results in more sustainable production due to lower energy requirements and waste generation. These processes entail anaerobic digestion and fermentation (microorganisms or their subcomponents) to generate biogas, methane, ethanol, and by-products like biofertilizers (Sadhukhan, Ng and Martinez 2014).

1.4.8 Chemical Processes

Chemical processes offer the conversion of biomass waste into specialty chemicals and bio-based polymers using pulping, hydrolysis, oxidation, hydrogenation, and transesterification. These processes alter the chemical composition of the feedstock. They may require elevated pressure, temperature, and the catalyst's maintenance to enhance the product's conversion yield and purity (Sadhukhan, Ng and Martinez 2014).

1.4.9 Physical or Mechanical Processes

Physical or mechanical processes are used primarily for size reduction, raw material densification, or component and product separation without altering the chemical composition of the biomass components (Sadhukhan, Ng and Martinez 2014).

1.5 Applications of Biomass Waste in the 21st Century

Biomass waste is harnessed for various uses in the 21st century, driven by the demand for sustainable resource management, renewable energy generation, and adverse environmental effects mitigation. Here are seven renowned modern-day applications for biomass waste.

1.5.1 Bioenergy Generation

Biogas: Biomass waste, such as sewage sludge, agricultural residue, organic food waste, and organic industrial waste, is anaerobically digested to manufacture biogas, a methane and carbon dioxide mixture. Biogas is a renewable energy source used to generate electricity and heat. (Maragkaki *et al.* 2018).

Biofuels: Three generations of biofuels have been generated. First-generation biofuels are derived from edible feedstock such as sugarcane, corn, rapeseed, and soybean; second-generation biofuels are derived from waste biomass and lignocellulosic feedstocks such as *Miscanthus*, Switchgrass, and Poplar (Ho, Ngo and Guo 2014). The main benefits are increased yields and fewer agricultural requirements (quality and quantity). The third generation of biofuels is derived from micro and macro algae. These biofuels are used as transportation fuels and are more environmentally friendly than fossil fuels (Daroch, Geng and Wang 2013).

1.5.2 Bio-Based Chemicals and Materials

Bioplastics: Biomass waste can produce bioplastics, which provide a sustainable alternative to traditional petroleum-based polymers. These bioplastics are often used for packaging retail products, and many other uses (Jõgi and Bhat 2020).

Bio-Based Chemicals: Biomass waste can be used as feedstock to make a variety of bio-based compounds, such as specialty chemicals, organic acids, and solvents applied in pharmaceuticals, fabrics and cosmetics (Yamakawa, Qin and Mussatto 2018).

1.5.3 Agricultural and Environmental Applications

Biofertilizers and Soil Amendments: Bioresidues from biomass waste processing, like anaerobic digestion, may be converted into nutrient-rich biofertilizers that increase soil quality and crop production. These bio-based organic fertilizers include a significant amount of live microbial biomass. Such microbial agents have a variety of applications, including soil improvement, nutrient replenishment, and crop conditioning, eventually supplying optimum nutrients for improved yields and productivity. Waste-derived biomass, such as algae, can be used as viable biofertilizers due to their promising nutritional content and important crop growth stimulators (Mahapatra, Satapathy and Panda 2022). Biochar, a carbon-rich substance from pyrolyzing biomass waste, is used as a soil supplement to enhance soil fertility, nutrition, and water absorption. It is not ideal to use heavy metal-polluted sludge-based biochar as a soil amendment because heavy metals will mobilize with biochar ageing (L. Wang *et al.* 2020).

1.5.4 Socio-Economic and Environmental Benefits

Biomass waste valorization is an essential component of circular bioeconomy approaches, in which waste products are converted into high-value products, completing the cycle and reducing resource depletion (Duan *et al.* 2022). With the utilization of biomass waste as a feedstock, industries can minimize their reliance on fossil feedstock and contribute to more sustainable manufacturing processes (Bos and Broeze 2020). Biomass waste can accelerate rural and disadvantaged economies through local job creation in biomass waste collection, procurement, allocation, and processing. Therefore, motivation for local advancement [of biomass waste] as a substitute for exports of low-cost products is widespread. (Lange *et al.* 2021). Small-scale biomass generators, such as biogas plants, could offer a decentralized energy supply to rural and underprivileged communities, decreasing reliance on centralized power grids (Hiremath *et al.* 2009). Some biomass waste valorization approaches, such as pyrolysis, can generate biochar, which sequesters soil carbon and reduces greenhouse gas emissions. Using biomass waste for energy decreases dependency on fossil fuels, which contribute considerably to CO2 emissions and global warming. Furthermore, the utilization of alternative fuels leads to improved waste management, such as diverting waste from landfills, minimized reliance on fossil fuels, and the prevention or reduction of environmental deformation caused by landfill operations, thus promoting sustainability and circular bioeconomy (Adesina 2020; U. Lee *et al.* 2023).

Conclusion

It is proposed that biomass waste feedstocks are a viable supply of natural elementary units and that reusing and recycling biomass waste might help to reduce environmental pressure. Furthermore, a broader perspective should be promoted to produce various materials (other than carbon) to allow the reuse and recycling of biomass waste. The emerging zero-waste biorefinery is critical in stimulating the development of bioproducts with low value. It should also be energy efficient and capable of utilizing all components, allowing various industrial sectors to produce environmentally beneficial and viable products with a low carbon and water footprint. Furthermore, the zero-waste biorefinery must evaluate potential accidental resource and feedstock competitions, water supply, product quality, land consumption, greenhouse gas emissions, and biodiversity impact. Various bioproducts and biofuels are manufactured while all intermediate values are minimized, and manufacturing expenses are lowered. The manufacturing process should isolate every constituent with significant yields, making additional purification or bioconversion easier. Energy requirements should be minimized throughout the production life cycle, and hazardous substances should be avoided. Furthermore, the process should be environmentally friendly with low carbon and water footprints.

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