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Review

Lignocellulosic Agricultural Waste Valorization to Obtain Valuable Products: An Overview

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Abstract: The sustainable management of lignocellulosic agricultural waste has gained significant attention due to its potential for the production of valuable products. This paper provides an extensive overview of the valorization strategies employed to convert lignocellulosic agricultural waste into economically and environmentally valuable products. The manuscript examines the conversion routes employed for the production of valuable products from lignocellulosic agricultural waste. These include the production of biofuels, such as bioethanol and biodiesel, via biochemical and thermochemical processes. Additionally, the synthesis of platform chemicals, such as furfural, levulinic acid, and xylose, is explored, which serve as building blocks for the manufacturing of polymers, resins, and other high-value chemicals. Moreover, this overview highlights the potential of lignocellulosic agricultural waste in generating bio-based materials, including bio-based composites, bio-based plastics, and bio-based adsorbents. The utilization of lignocellulosic waste as feedstock for the production of enzymes, organic acids, and bioactive compounds is also discussed. The challenges and opportunities associated with lignocellulosic agricultural waste valorization are addressed, encompassing technological, economic, and environmental aspects. Overall, this paper provides a comprehensive overview of the valorization potential of lignocellulosic agricultural waste, highlighting its significance in transitioning towards a sustainable and circular bioeconomy. The insights presented here aim to inspire further research and development in the field of lignocellulosic waste valorization, fostering innovative approaches and promoting the utilization of this abundant resource for the production of valuable products.

Keywords: lignocellulose; agriculture waste; value-added products

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1. Introduction

The potential consequences of the climate crisis and the effects it has already triggered are prompting an intensive examination of the necessity of and possibilities for reducing anthropogenic greenhouse gas (GHG) emissions [1]. There is a direct physical relationship between the quantity of raw materials used in industrial processes, the energy required, and hence, GHG emissions [2]. The use of renewable raw materials can contribute to slowing down climate change by releasing fewer greenhouse gases than fossil fuels when used for energy and even by binding carbon dioxide in the long term when used for materials [3–5].

The most abundant renewable raw material is lignocellulosic biomass, with an annual global production of about 182 billion tons, of which "only" about 8 billion tons are currently used [6]. Lignocellulosic biomass includes plants and waste from their treatment, such as agricultural and paper mill waste. This biomass contains three of the most abundant natural polymers on the planet, cellulose, lignin and hemicellulose, which can be used for

the preparation of bioplastics, with or without functionalization, or used for the synthesis of chemical compounds [7,8].

The Waste Framework Directive (WFD) seeks to convert linear economic processes into circular ones, transforming the European Union (EU) into a recycling society [9,10].

The target of the WFD is to protect the environment by drastically reducing the indiscriminate use of resources to save human health, all by implementing better techniques for waste management, such as recovery and recycling [11].

To achieve these goals, the WFD proposes to replace linear economy processes with others based on the circular economy.

The concept of the circular economy emerged in 2015 as a response to the environmental impacts and economic costs generated via waste management. It proposes transforming linear material flows, which follow a resource-product-waste pattern, into circular flows based on resource-recycled product-resources. In the linear economy model, waste management relies on disposal in controlled locations or incineration, whereas the circular economy aims to reduce, recycle, and reuse these waste materials [12,13]. Removing waste from the industrial chain by repurposing it as a recycled resource results in cost savings in terms of raw materials and reduces dependence on primary resources. This is particularly significant given the intensification of climate change, increasing global population, and urbanization [14].

Cellulose, lignin, and hemicellulose are the primary components of lignocellulosic biomass derived from natural plants. They are characterized by their abundance, renewability, biodegradability, and biocompatibility, making them highly valuable in various commercial applications. These properties suggest that with proper management, it may be possible to reduce our society's current dependence on fossil resources. However, natural lignocellulosic materials exhibit low solubility and processability, which limits their effective and practical utilization. Therefore, pre-treatments are generally required to enable their subsequent use as an energy source or renewable resource [15,16].

Cellulose is a biopolymer composed of D-glucose monomers linked by ß-1,4-glycosidic bonds with cellobiose as the fundamental repeating unit held together by hydrogen bonds and van der Waals forces, imparting crystallinity and resistance to water swelling and enzymatic attacks [17–19]. It has been described that under high temperature and pressure, water can disrupt the hydrogen-bonded crystalline structure and hydrolyze the ß-1,4-glycosidic bond, leading to the production of glucose monomers [16,20–22].

In contrast, hemicellulose contains fewer repeating ß-1,4-glycosidic bonds and exhibits a more random structure, resulting in lower crystallinity and reduced resistance compared to cellulose. Hemicellulose is a polysaccharide composed of D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-O-methylglucuronic acid, D-galacturonic acid, and D-glucuronic acid. These monomers are connected not only by ß-1,4-glycosidic bonds but also by ß-1,3-glycosidic bonds, leading to a branched structure that renders hemicellulose more susceptible to hydrothermal extraction or hydrolysis than cellulose. Lignin, on the other hand, is an amorphous heteropolymer composed of phenylpropane units linked via various bonds [23–25].

Several management strategies have been studied aiming to minimize the high quantities of lignocellulosic residues generated, promoting their reuse and recycling [26,27]. Limarta et al. have published interesting studies on the effective depolymerization of lignin using various catalytic approaches, such as a carbon-supported ruthenium catalyst in ethanol/formic acid or a combination of metallic catalysts and bases in supercritical ethanol [28,29]. Bijoya Devi et al. have published an intriguing study on how to add value to various lignocellulosic wastes, particularly by employing them in the cultivation of fungi for the production of mushrooms and other high-value products derived from them [30]. Furthermore, Karadirek and Okkay have developed a statistical model to produce activated carbon using spent mushroom compost [31]. Kim et al. [32] have developed the pyrolysis of Kraft lignin in a rotary kiln reactor, thus suppressing carbon agglomeration, and Trinh et al.

have published interesting pretreatment strategies to optimize bioethanol production and its concentration via pervaporation [33].

The production of biofuels from lignocellulosic waste is the subject of several studies [11,16,34–38]. In addition to biofuels, lignocellulosic waste has proven to be an excellent feedstock for chemical production [39–43]. Finally, the literature includes several studies on the creation of a true biorefinery starting from forest residues to achieve a circular bioeconomy [43–49].

In the context of a circular economy, the traditional management of lignocellulosic waste, based on grinding and compacting, which reduced management costs but not environmental impact, is no longer current or cost-effective. Recycling lignocellulosic waste as a byproduct or via composting, energy valorization, biofuel production, synthesis of glucose and other high-value products, and the synthesis of biopolymers, biocomposites, nanofibers, and nanoparticles are interesting alternatives that align well with the circular economy. The development of processes to convert lignocellulose into valuable chemicals, polymers, and energy is crucial for utilizing renewable sources. It is indeed the role of renewable sources to replace traditional fossil fuels and the chemicals derived from them, and lignocellulosic biomass is a valuable feedstock for these processes as it does not compete with food production [50–56].

The main objective of this work is to provide a comprehensive overview of technologies for the recovery of lignocellulosic waste, focusing the analysis from the perspective of the circular economy in general and the biorefinery in particular. Under this vision, special attention will be given to the great potential of lignocellulosic biomass as a new energy source and a renewable resource for the synthesis of chemicals and other high-value-added materials.

2. Energetic Valorization of Lignocellulosic Biomass

Lignocellulosic biomass, derived from plant cell walls, has gained significant attention as a promising renewable energy source due to its abundance, low cost, and potential to mitigate greenhouse gas emissions [57]. The increasing demand for sustainable and carbon-neutral energy solutions has driven extensive research on the efficient conversion of lignocellulosic biomass into valuable energy products [58,59].

Brownstein [60] has described various sources of renewable motor fuels, such as ethanol, isobutanol, natural gas, and biodiesel, along with their production processes, specific properties, and economic advantages and disadvantages. As an advantage, this author states that lignocellulosic waste avoids the food-versus-fuel competition found in other renewable fuel sources, such as corn starch, and that they are abundant as they constitute 50% of the woody structure of plants.

Similar outcomes have been shown by Ullah et al. [61], who studied the current status, limitations, and challenges of biofuel production from lignocellulosic biomass as a renewable energy alternative to carbon-based fossil fuels, highlighting the advantage that biomass is not in competition with food demand. Although the energy currently produced from biomass is limited, the International Energy Agency has estimated that lignocellulosic biomass could be the primary source of global energy demand by 2030 [62–64].

This biomass type is composed of cellulose, hemicellulose, and lignin, with each component presenting unique challenges and opportunities for effective valorization [65,66]. The valorization of lignocellulosic biomass involves a series of physical, chemical, and biological processes to convert its complex structure into high-energy-density fuels and chemicals [67–69].

Various pre-treatment techniques have been developed to enhance the accessibility of cellulose and hemicellulose, followed by conversion processes such as pyrolysis, gasification, and enzymatic hydrolysis [65,70,71]. Although significant advancements have been made, there are still technical and economic barriers that need to be overcome for the large-scale implementation of lignocellulosic biomass valorization [72–74]. Figure 1 shows a schematic representation of the main technologies to exploit for energy purposes lignocel-

lulosic biomass. The main technologies used and the various steps of each are summarized via a block diagram. This paragraph provides an overview of the recent advancements, challenges, and potential solutions in the energetic valorization of lignocellulosic biomass, with a focus on improving process efficiency, product selectivity, and overall sustainability.

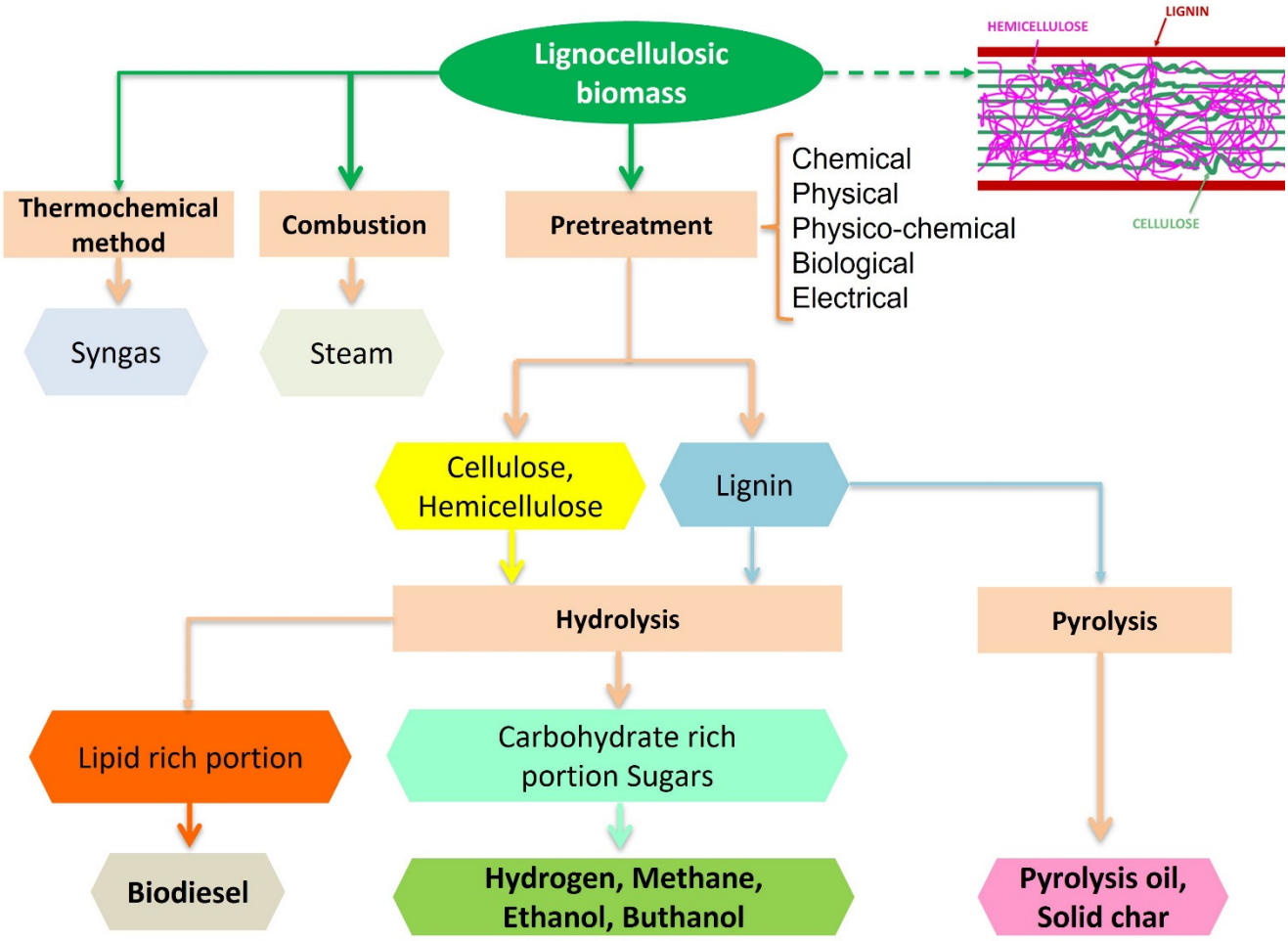

Figure 1. The main technologies for an energetic valorization of lignocellulosic biomass.

2.1. Bioethanol

Bioethanol is the world's most abundant biofuel and is being considered an alternate substitute in gasoline and other transportation industries. Ethanol is also an important precursor and an excellent organic solvent to synthesize numerous valuable chemicals and other composites [75]. As a matter of fact, bioethanol is a historically significant product derived from lignocellulosic biomass, and therefore, it deserves a more detailed study. Bioethanol production can be achieved by hydrolyzing a wide range of carbohydrate-rich renewable materials into fermentable sugars, which are, in turn, converted into ethanol. Depending on the raw material from which it is derived and its manufacturing process, bioethanol can be classified into three different generations. First-generation (1-G) bioethanol is obtained via yeast fermentation of sucrose crops intended for use in human food or animal feed, such as sugarcane (juice, molasses), grains (maize, wheat), and tuber crops (potato, sugar beet) [76]. Second-generation (2-G) bioethanol is made from lignocellulosic raw materials, including no-food plants, such as switchgrass and trees, and residual materials (such as solid waste, municipal waste, wood processing residues, and agricultural waste) [77].

Lastly, algal biomass is used to produce third-generation (3-G) bioethanol [78].

2 g and 3 g bioethanol is also known as advanced bioethanol. Technologies and mechanisms for advanced bioethanol production are still in the research and development stage or in the pilot or adaptation stage for large-scale production [79].

Despite the controversy over food competition and negative impacts on the environment and land use, 1G-bioethanol still accounts for more than 95% of the global ethanol market [80].

However, the growing demand for bioethanol, combined with the increase in population, raises concerns about 1G bioethanol's long-term sustainability. In fact, it competes with food supplies for human and animal consumption, aggravating problems regarding food security worldwide, land and water availability, as well as soil contamination from distillation residues [81]. Furthermore, because of the increasing production of food commodities, significant quantities of agro-industrial waste are generally untreated and disposed of as waste via burning, dumping, or unplanned landfilling, resulting in environmental pollution, public health problems, and decreased organic matter in the soil [82]. The valorization of agricultural residues for 2 g bioethanol production leads to environmental benefits.

Lignocellulose biomass mainly consists of cellulose fibers embedded in a matrix of hemicelluloses and lignin [83,84]. Cellulose, accounting for 40–50% of agro-industrial residues, is an insoluble homopolysaccharide composed of fermentable sugars and formed via β-D-pyranose units linked by glycosidic bonds. About 40% of agro-industrial residues are hemicellulose, which contains pentoses, hexoses, and uronic acids. Lignin is the most complex natural polymer, formed via the cross-linking of three major components: p-coumaric, coniferyl, and sinapyl alcohols. It ensures the mechanical strength of the cell wall as a whole and makes up between 20–30 wt% of agro-industrial waste [82,83,85]. In agro-industrial waste generated from different sources, biomass constituents can vary significantly (Table 1) [83].

Table 1. Composition of major compounds in most common agro-industrial waste.

Composition (% dry wt)	Rice Straw	Rice Husk	Wheat Straw	Corn/Maize Stalks	Sugarcane Bagasse	Soybean Straws	Barley Straw	Reference
Cellulose	46.60 ± 10.40	37.50 ± 7.50	41.45 ± 8.55	37.30 ± 2.30	43.60 ± 11.60	63.50 ± 19.50	32.50 ± 1.50	[32,34,35]
Hemicellulose	26.00 ± 7.00	22.00 ± 3,00	25.25 ± 10.25	25.90 ± 9.10	27.15 ± 17.15	22.43	26.50 ± 2.50	[32,34,36]
Lignin	17.00 ± 9.00	16.00 ± 8.00	12.60 ± 7.38	12.70 ± 5.70	17.65 ± 7.65	9.50 ± 4.50	14.50 ± 0.50	[32,34,35,37]

The bioconversion of lignocellulose biomass into 2 g bioethanol requires three key steps: pretreatment, saccharification (or hydrolysis), and fermentation [84,86].

Pretreatment of lignocellulose biomass is essential to reduce the biomass size, solubilize, hydrolyze, and separate the cellulose, hemicellulose, and lignin components [16,87–89]. A variety of pretreatment methods are available (physical, chemical, physiochemical, biological, electrical, or a combination thereof) [15,83] (Table 2).

Table 2. Methods for lignocellulose biomass pretreatment.

Physical	Chemical	Physio-Chemical	Biological	Electrical
Milling Extrusion Microwave Ultrasound	Acid hydrolysis Alkaline hydrolysis Organosolv Ozonolysis Wet oxidation CELF DESs	Steam explosion AFEX ARP CO_2 explosion SCFs Liquid hot water	Live microbes Enzymes	PEF

CELF: co-solvent enhanced lignocellulosic fractionation; DESs: deep eutectic solvents; AFEX: ammonia fiber explosion; ARP: ammonia recycle percolation; SCFs: supercritical fluids; PEF: pulsed-electric field. Adapted from [69,90].

Following pretreatment, lignocellulosic biomass usually undergoes saccharification, which is usually carried out with lignocellulolytic enzymes that can break down lignocellulose biomass into its monomers [91,92].

Lignocellulolytic enzymes occur in several Fungi and Bacteria [93], and they are divided into two categories: hydrolases (cellulases, hemicellulases, xylanases, proteases, and amylases) that break down cellulose chains and ligninases that break down lignin chains [94]. Because of their high specificity and ability to work in mild conditions, lignocellulolytic enzymes deriving from microbes are more efficient than inorganic catalysts. However, several factors limit their use in industrial processes, including their low stability at high temperatures, the high cost of isolating and purifying them, and their difficulty in retrieving them from reaction mixtures [25,95].

Fermentation-based bioconversion of lignocellulose biomass has been investigated using a variety of microorganisms. One of the most used yeasts for CR fermentation is Saccharomyces cerevisiae [96].

However, several studies have shown that Fungi belonging to the genera *Aspergillus*, *Fusarium*, *Rhizopus*, *Monilia*, *Neurospora*, *Trichoderma*, and *Paecilomyces*, as well as Bacteria, especially *Lactobacillus* sp. (*Lactic Acid Bacteria*, LAB), *Clostridium*, and *Bacillus* sp., can ferment monomeric sugars from CRs into a variety of valuable compounds [25,96,97].

Lignocellulosic feedstock fermentation varies depending on the microorganisms and raw materials. Five types of microbial cultures are used in fermentation processes, as summarized in Table 3.

Table 3. Microbial cultures used in fermentation process.

Microbial Culture	Examples of Typical Microbial Cultures Involved	Description	Culture Condition Used	Refs.
Pure culture	*Saccharomyces cerevisiae*	One type of microorganism developed from a single cell	Not available	[98]
Co-culture	*Aspergillus niger* and *Candida shehatae*	Growths from two distinct cell types	pH: 5.89; Fermentation time: 3.6 days; Temperature: 28 °C	[99]
Mixed culture	*Paenibacillus* sp. and four strains of *Zymomonas mobilis*	Growths from more than two microorganisms	pH: 5–6 Fermentation time: 120 h;	[100]
Immobilized culture	*Zymomonas mobilis*	A given matrix traps a type of microorganism	pH: 3.8–7.65	[101]
Co-immobilized culture	*Zymomonas mobilis* and *Pichia stipitis*	A given matrix traps two distinct types of microorganisms	pH: 7; Fermentation time: 24 h; Temperature: 50 °C	[102]

There are several strategies for fermentation-based bioconversion of lignocellulose biomass via microbes: separate enzymatic hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), consolidated bioprocessing (CBP) [25].

In SHF, saccharification (or enzymatic hydrolysis) and fermentation reactions take place in different bioreactors. In SSF, SSCF, and CBP technologies, enzyme hydrolysis and fermentation are combined into one reactor to reduce overall production time, operating costs, and inhibitors, as well as improve the hydrolysis rate [103].

SHF is the predominant fermentation strategy, even if it has numerous disadvantages, including the high production cost due to long processing times and expensive equipment [104]. In addition, because of SHF's long duration, it is susceptible to microbial contamination [105]. The released sugars, primarily cellobiose and glucose, inhibit the hydrolytic enzyme activity. Approximately 6 g/L of cellobiose reduces enzyme activity by 60%. Contamination could also be caused by enzymes [106].

SSF combines enzymatic hydrolysis and fermentation in one reactor [107], and it has several advantages compared to SHF. In the first place, the use of a single vessel for fermentation and saccharification reduces residence times and capital costs. In addition, the inhibitory compounds from enzymatic hydrolysis are reduced, improving the overall efficiency of the process [108–110].

A significant drawback of SSF limiting its use on an industrial level compared to the SHF is the different optimal temperatures and pH for hydrolysis and fermentation. Indeed, the optimal temperature of enzymatic hydrolysis is typically greater than the fermentation

temperature. Consequently, a proper equilibrium point must be found for the process to work [111]. Currently, several thermotolerant bacteria and yeasts (i.e., *Candida acidothermophilum* and *Kluyveromyces marxianu*) have been investigated for increasing fermentation temperatures, approaching optimal hydrolysis temperatures [112]. Another obstacle to SSF is the difficulty of implementing continuous fermentation by recirculating and reusing the fermenting microbes [83]. As a result, yield losses in SSF processes constitute an inherent weakness [113].

SSCF allows the fermentation of both hexoses and pentoses in a single bioreactor [114], reducing energy consumption and process costs compared to using SSF, resulting in higher efficiency [115]. A major drawback of the SSCF process is the difference in temperature, pH, and other conditions between hydrolytic enzymes and fermentative microorganisms, as well as between microorganisms used in co-fermentation [116]. Thermophilic microorganisms can be engineered for this purpose [115].

In CBP, enzymes are produced in a single bioreactor via a single microorganism community. In this process, also known as direct microbial conversion (DMC), fermentation, saccharification, and hydrolytic enzyme production are performed in a single step, reducing operational costs and capital investments. For this purpose, several thermophilic cellulolytic anaerobic bacteria are investigated, including *Thermoanaerobacter ethanolicus*, *Clostridium thermohydrosulfuricum*, *Thermoanaerobacter mathranii*, *Thermoanaerobium brockii*, *Clostridium thermosaccharolyticum strain*. [117]. Currently, numerous studies focus on identifying and exploiting mixed cultures able to hydrolyze lignocellulosic biomass simulta neously with fermentation [118].

2.2. Biomethane

Biomethane production from lignocellulosic biomass offers a promising avenue for sustainable and renewable energy generation. Lignocellulosic biomass, composed of cellulose, hemicellulose, and lignin, is an abundant and widely available feedstock that can be effectively utilized for biomethane production via anaerobic digestion [119]. Anaerobic digestion is a biological process in which microorganisms break down complex organic matter in the absence of oxygen, resulting in the production of biogas, primarily composed of methane (CH_4) and carbon dioxide (CO_2) [120]. Lignocellulosic biomass presents unique challenges due to its complex structure and resistance to degradation. However, efficient pre-treatment methods have been developed to enhance the accessibility of the biomass components, such as steam explosion, alkali treatments, and enzymatic hydrolysis [71]. These pre-treatment techniques facilitate the breakdown of complex polymers and increase the bioavailability of substrates for microbial conversion, leading to improved biomethane yields.

The crystallinity of cellulose is reduced, and the porosity of cellulose is increased via various methods such as acid, base, and enzymatic hydrolysis, biological treatment, and steam explosion, which remove lignin and hemicellulose. [15,121,122].

The anaerobic digestion process involves a diverse consortium of microorganisms, including bacteria, archaea, and fungi, working synergistically to convert lignocellulosic biomass into biomethane [123]. The microorganisms hydrolyze the complex carbohydrates into simple sugars, ferment them into organic acids, and subsequently convert them into methane and carbon dioxide via methanogenesis. The process conditions, such as temperature, pH, and substrate concentration, need to be carefully controlled to optimize microbial activity and ensure efficient biomethane production [124].

Buitron et al. [125] studied the waste generated in the hydrothermal pretreatment (HPT) process. This waste is rich in organic matter, which can be used to produce methane via anaerobic digestion processes. The generation of methane from HPT waste via anaerobic digestion has economic and environmental benefits, but the efficiency of this process is low due to inhibitory compounds generated during biomass pretreatment, such as furan and lignin derivatives (phenolic compounds). The authors of this study evaluated the biodegradability rate and the theoretical biochemical methane potential (BMP) of the waste

material obtained from HPT lignocellulose pretreatment, its composition and structure, and hydrolysis rates. Their results revealed that sugarcane has the highest organic matter content per mass of biomass and, therefore, the highest BMP and degradability. They also demonstrated that the liquid fraction produced higher BMP values than the solid fraction and that the relatively low biodegradability of HPT waste compared to natural carbohydrates is due to an inhibitory effect of furfural and lignin. However, at lower concentrations, furfural has an inhibitory effect, which becomes stimulating at high concentrations; therefore, the addition of furfural optimizes biomethane production [11,125]. As a matter of fact, Differences in furfural content in steam-exploded hydrolyzates are responsible for different degrees of inhibition of anaerobic digestion. Furfural concentrations ranging from 100 to 500 mg/L inhibited methane production, but a concentration of 1000 g/L had a stimulating effect on anaerobic digestion [125,126]. Mwene–Mbeja et al. [127] investigated the detailed mechanisms of the enzymatic reactions that transform residual proteins, carbohydrates, and lipids into biomethane and fertilizers as a strategy to improve the efficiency of biomethanation in industrial applications, thereby maximizing biomethane production or biofertilizer quality. These authors investigated the function of various types of enzymes in organic reactions that occur during anaerobic digestion, such as hydrolysis, acidification, acetate synthesis, and methane synthesis. Each type of substrate (proteins, carbohydrates, or lipids) is degraded under anaerobic conditions via specific enzymes, and the intermediates are substrates for the production of methane and fertilizers [127].

To improve biomethane yields, co-digestion strategies have been explored by co-feeding lignocellulosic biomass with other organic substrates, such as animal manure, food waste, or energy crops [128]. Co-digestion enhances the nutrient balance, improves the carbon-to-nitrogen ratio, and increases the diversity of microbial communities, leading to more stable and efficient biomethane production. Furthermore, process optimization via reactor design, operational parameters, and control strategies has been investigated to maximize biomethane production from lignocellulosic biomass [129].

In addition to biomethane production, the anaerobic digestion process offers the additional benefits of waste treatment and nutrient recycling. The digestion residues, known as digestate, can be used as a nutrient-rich fertilizer, thereby closing the loop in a sustainable and circular bioeconomy [120]. Moreover, the utilization of lignocellulosic biomass for biomethane production contributes to reducing greenhouse gas emissions and dependence on fossil fuels.

In summary, biomethane production from lignocellulosic biomass holds great potential as a renewable energy pathway. Pre-treatment methods, process optimization, and co-digestion strategies are being continuously researched and developed to enhance the efficiency and economic viability of biomethane production. The utilization of lignocellulosic biomass not only offers a sustainable energy source but also provides waste management solutions and contributes to environmental sustainability.

2.3. Biodiesel

The production of biodiesel from lignocellulosic biomass holds great promise as a renewable and sustainable alternative to fossil fuels. In fact, many nations have limited biodiesel production due to the vast land area required for cultivating oilseed crops and the competition of energy crops with traditional food crops [130]. As a result, research has focused on biodiesel production from waste elements such as used oils, food residues, and residual biomass [131–135].

Lignocellulosic biomass, composed of cellulose, hemicellulose, and lignin, is a widely available and abundant feedstock that can be effectively utilized for biodiesel production via various conversion pathways [136]. The complex structure and recalcitrant nature of lignocellulosic biomass require appropriate pretreatment methods to enhance the accessibility of biomass components and facilitate subsequent conversion processes [137]. Physical, chemical, and biological pretreatment methods have been explored to break down the complex structure, remove impurities, and improve enzymatic hydrolysis efficiency [138].

Physical pretreatment methods increase the surface area and enhance the accessibility of cellulose and hemicellulose to enzymes [38]. Chemical pretreatment methods help to disrupt the lignin matrix and solubilize hemicellulose, facilitating enzymatic hydrolysis and subsequent biodiesel production [139]. Biological pretreatment methods offer the potential for selective lignin degradation and improved enzymatic hydrolysis [140–145].

Enzymatic hydrolysis is a key step in biodiesel production from lignocellulosic biomass, where cellulose and hemicellulose are enzymatically converted into fermentable sugars. Cellulases and hemicellulases are commonly employed enzymes in this process, breaking down polysaccharides into monomeric sugars suitable for fermentation [146,147]. Selection and optimization of enzyme cocktails, including cellulases, hemicellulases, and accessory enzymes, are essential to achieve efficient hydrolysis and maximize sugar yields [148–151]. Enzyme loading, hydrolysis conditions (temperature, pH), and substrate composition significantly influence hydrolysis efficiency and subsequent biodiesel production [152–154].

The fermentation of liberated sugars into biodiesel can be realized via microbiological processes, such as yeast fermentation or microbial consortia. Yeasts, such as Saccharomyces cerevisiae, are commonly used for ethanol production from lignocellulosic biomass, which can be subsequently converted into biodiesel via transesterification reactions [155–157]. Alternatively, microbial consortia, including bacteria and archaea, have been investigated for the direct production of biodiesel from lignocellulosic sugars via the fermentation pathway [158–160]. The choice of microorganisms, fermentation conditions, and downstream processing stages significantly affect the yield and quality of the produced biodiesel [161].

Recently, emerging biofuels such as renewable diesel have gained attention, which are obtained by hydro-deoxygenating renewable resources such as biodiesel, vegetable oils, and single-cell oils. In addition to green diesel, renewable diesel is also known as second-generation biodiesel, which exhibits superior cleanliness, oxidative stability, and cold compatibility, giving renewable diesel a competitive advantage over conventional biodiesel created via transesterification [162]. Renewable biodiesel can reduce nitrogen oxide and hydrocarbon emissions, while biodiesel reduces carbon dioxide emissions and other particulate matter. The existing petroleum-based refining infrastructure can be utilized for the production and distribution of renewable diesel. In addition to traditional methods, hydrodeoxygenation is an efficient method for reducing the viscosity of triacylglycerols [163].

To improve the overall efficiency and economics of biodiesel production from lignocellulosic biomass, integrated biorefinery approaches have been proposed. These approaches aim to maximize the utilization of various biomass components, such as lignin and hemicellulose, to produce high-value products alongside biodiesel. Lignin, a byproduct of lignocellulosic biomass pretreatment, can be valorized into valuable chemicals, biofuels, or high-quality materials, reducing waste and improving the process's overall economy [164]. Furthermore, the utilization of hemicellulose, a byproduct of cellulose hydrolysis, to produce basic chemicals or biopolymers further enhances the sustainability and value proposition of the biorefinery concept [165].

In summary, biodiesel production from lignocellulosic biomass offers a promising opportunity for renewable and sustainable energy. Studies are ongoing on pretreatment methods, enzymatic hydrolysis, fermentation pathways, and integrated biorefinery approaches to improve the efficiency, yield, and sustainability of the process. Further research and optimization are needed to address technical and economic challenges and facilitate the commercialization of biodiesel production from lignocellulosic biomass.

2.4. Hydrogen and Jet Fuel

The production of hydrogen and jet fuel from lignocellulosic biomass holds significant potential as a sustainable and renewable energy solution for industry in general and the aviation sector in particular. Lignocellulosic biomass, derived from agricultural residues, energy crops, and forestry by-products, offers a plentiful and diverse feedstock for the production of both hydrogen and jet fuel [166,167]. Recent advancements in conversion technolo-

gies, such as thermochemical and biochemical processes, have shown promise in efficiently extracting hydrogen and synthesizing renewable jet fuel from lignocellulosic biomass.

Thermochemical processes, including gasification and pyrolysis, have gained attention for hydrogen and syngas production. Gasification, a process in which biomass is heated in the presence of a controlled amount of oxygen or steam, converts the lignocellulosic biomass into a mixture of hydrogen, carbon monoxide, and other gases [168–171]. Syngas obtained from gasification can be further processed to extract hydrogen via a water–gas shift reaction or utilized for the synthesis of liquid hydrocarbon fuels, including jet fuel, via Fischer–Tropsch synthesis [172–175]. Pyrolysis, on the other hand, involves the thermal decomposition of biomass in the absence of oxygen, producing a bio-oil that can be subsequently upgraded to obtain hydrogen-rich gases and liquid hydrocarbon fuels [176].

Biochemical routes, such as biological and enzymatic processes, offer an alternative approach to hydrogen and jet fuel production from lignocellulosic biomass. Biological pathways, including dark fermentation and photo-fermentation, utilize microorganisms to produce hydrogen by fermenting biomass sugars or volatile fatty acids derived from lignocellulose hydrolysis [177,178]. These processes can be optimized by selecting appropriate microorganisms, optimizing process conditions, and integrating co-cultures to enhance hydrogen yields and productivity. Enzymatic processes, employing cellulases and other hydrolytic enzymes, can effectively hydrolyze cellulose and hemicellulose fractions of lignocellulosic biomass into fermentable sugars, which can then be converted into hydrogen via microbial fermentation or further processed into jet fuel precursors [75,179,180].

Dark fermentation of lignocellulosic biomass has been shown to produce biohydrogen, a key component of renewable natural gas, along with other by-products such as methane, butyrate, acetate, and ethanol, depending on the specific microbes and operational conditions [181–183]. To optimize biohydrogen productivity and yield, various strategies have been explored, including sequential saccharification and fermentation, consolidated bioprocessing, separate hydrolysis and fermentation, and cell-free biocatalytic synthesis [184,185]. Several factors influence biohydrogen production, including nutrient availability, raw materials, temperature, and pH [186,187]. Typically, a combination of mixed substrates and microbial cultures is employed, often in conjunction with nanotechnology and carbon-biomaterials, to promote microbial growth and enhance the activity of enzymes involved in hydrogen production [188–190]. These approaches offer potential avenues for improving the efficiency and effectiveness of biohydrogen production from lignocellulosic biomass.

The production of biokerosene for aviation fuel (commonly referred to as jet fuel) involves a combination of biochemical and thermochemical processes, with vegetable oil being a primary feedstock [191,192]. However, due to concerns regarding the use of food crops for fuel production, there has been a growing focus on identifying alternative feedstock materials and exploring other biorefining pathways [193]. Lignocellulosic biomass can serve as a viable feedstock for the production of biokerosene via thermochemical conversion processes. In this approach, the feedstock is directly converted into sugars, which are then synthesized into biokerosene. The process typically involves a pretreatment step to obtain intermediate products, which are subsequently upgraded into biokerosene [194,195]. However, the high selling price of biokerosene remains a challenge that hinders its widespread commercialization [192]. Efforts are ongoing to address the cost-effectiveness and scalability of biokerosene production from lignocellulosic biomass, aiming to overcome these barriers and facilitate its broader adoption in the aviation industry.

To overcome the challenges associated with lignocellulosic biomass conversion, various research efforts have focused on improving process efficiency, feedstock availability, and cost-effectiveness. Advancements in catalyst development, process integration, and reactor design have shown promise in enhancing the conversion efficiency of lignocellulosic biomass into hydrogen and jet fuel [196–198]. Additionally, advancements in feedstock preprocessing, such as fractionation and pretreatment methods, have facilitated the extraction of key components from lignocellulosic biomass and improved the overall process economics [15,69,199–201].

Furthermore, the development of sustainable supply chains and the utilization of advanced feedstock sourcing methods have been explored to ensure the availability of lignocellulosic biomass for hydrogen and jet fuel production. Strategies such as agricultural residue management, dedicated energy crop cultivation, and utilization of forest residues contribute to the sustainable sourcing of biomass feedstocks and minimize the potential environmental impacts [202–204].

In summary, the production of hydrogen and jet fuel from lignocellulosic biomass presents an environmentally friendly and renewable pathway for the aviation industry. Thermochemical and biochemical conversion technologies, along with advancements in catalysts, reactors, and feedstock sourcing, are driving progress in the efficient and cost-effective production of hydrogen and jet fuel from lignocellulosic biomass. Continued research and development efforts are crucial to further optimize these processes and enable their commercial implementation.

2.5. Biobuthanol and Biogas

Utilizing lignocellulosic biomass for the production of biobutanol and biogas presents a sustainable and renewable alternative to conventional fuels. Lignocellulosic biomass, including agricultural residues, forestry waste, and energy crops, serves as a promising feedstock for biofuel production, such as biobutanol [205]. The biobutanol industry yields a diverse range of value-added by-products, encompassing fibers, solvents, coatings, and plastics, and acts as a precursor for various allied chemicals, such as butyl acetate, acrylic acid, and adhesives, fostering economic growth via a wide array of products [206,207]. Biobutanol can be generated via a two-step fermentation process known as acetone–butanol–ethanol (ABE) fermentation. By subjecting a variety of biomass feedstocks to solventogenic *Clostridium* species fermentation, the industrial acetone–butanol–ethanol fermentation process enables biobutanol production. Initially, lignocellulosic biomass undergoes pretreatment and enzymatic hydrolysis, releasing sugars that are subsequently fermented via solvent-producing microorganisms to yield biobutanol [208–211]. Recent advancements in the ABE fermentation process involve the development of genetically modified microorganisms with enhanced capabilities for biobutanol production [75,211,212]. However, the acetone–butanol–ethanol process encounters challenges such as low yield, increased toxicity of butanol to microbes, and difficulties in downstream recovery of butanol. Compared to petrochemical-based butanol production ($1.50/kg), biobutanol produced via acetone–butanol–ethanol fermentation yields a fuel price of $1.80/kg. Hence, future research strategies should focus on reducing the cost of biobutanol processing via cutting-edge genetic manipulation techniques [212–214].

Researchers have explored various approaches to biobutanol production from lignocellulosic biomass. For instance, Moradi et al. achieved a biobutanol yield of 112 g per kilogram of alkali-/acid-pretreated rice straw [215]. Another study utilized *Clostridium* sporogenes in the acetone–butanol–ethanol fermentation of detoxified, enzyme-hydrolyzed, and acid-pretreated rice straw, achieving optimal biobutanol production and a productivity rate of 0.05 g/L per hour [216]. A two-stage fermentation process involving acidogenic fermentation followed by acetone–butanol–ethanol fermentation resulted in a biobutanol production rate of 0.5 g/L per hour using pretreated rice straw [217]. Mild alkali pretreatment and enzymatic hydrolysis of rice straw prior to acetone–butanol–ethanol fermentation demonstrated an efficacy range of biobutanol production from 0.53 to 2.93 g/L [218].

Anaerobic digestion of lignocellulosic biomass provides a pathway for the generation of biogas, predominantly composed of methane and carbon dioxide. This biological process involves microbial consortia transforming biomass via anaerobic conditions, resulting in the production of methane-rich biogas [219,220]. Several factors impact the efficiency of biogas production, including biomass composition, operating conditions, and microbial activity. Strategies such as co-digestion, which involves blending different biomass types, and thermal pretreatment methods have been investigated to enhance biogas yields [221–223]. Advances in anaerobic digestion technology, including high-rate digesters and microbial enrichment techniques, have contributed to improved process performance and methane

production [224]. Various factors, such as pH, temperature, organic loading rate, retention time, and carbon-to-nitrogen ratio, exert cumulative effects on the efficiency of biogas production techniques. The utilization of psychrophilic, mesophilic, and thermophilic microorganisms in the bioreactor, depending on their temperature sensitivity, is crucial for anaerobic digestion [225]. However, the recalcitrant structure of lignocellulosic biomass poses challenges for effective anaerobic digestion. Further investigation into co-digestion processes and different pretreatment methods is necessary to enhance microbial growth and improve the biogas production rate [226].

The integration of biobutanol and biogas production from lignocellulosic biomass offers synergistic benefits. By utilizing the by-products of biobutanol fermentation, such as residual sugars and lignin, as substrates for biogas production via anaerobic digestion, the overall energy efficiency and valorization of lignocellulosic biomass can be enhanced. This integrated approach contributes to a more sustainable and economically viable bioenergy production system [227–229].

2.6. Gasification and Pyrolysis

Gasification and pyrolysis of lignocellulosic biomass are promising thermochemical conversion technologies that offer sustainable and efficient routes for the production of valuable biofuels and bioenergy. Lignocellulosic biomass, including agricultural residues, forest waste, and energy crops, represents a vast and renewable resource for bioenergy production [230,231]. Gasification is a process that converts solid biomass into a mixture of combustible gases, primarily carbon monoxide (CO), hydrogen (H2), and methane (CH4), known as syngas, via high-temperature reactions in an oxygen-limited environment [232,233]. Pyrolysis, on the other hand, involves the thermal decomposition of biomass in the absence of oxygen, leading to the formation of liquid bio-oil, solid char, and non-condensable gases [234].

As highlighted in Section 2, Brownstein [60] explored the production of synthesis gas from lignocellulosic feedstock as a means of utilizing basic fuels. Initially, industries favored treatment and fermentation as the primary processes for valorizing lignocellulose waste, but some have since shifted towards converting it into synthesis gas. While gasification of fossil fuels is a well-established technique, utilizing lignocellulose waste as a raw material for synthesis gas production enables the use of carbon sources to generate liquid fuels.

Several prominent companies, including Lanzatech, Ineos, Coskata, and Syntec Biofuels, are engaged in gas synthesis applications such as the Fischer–Tropsch method, the ExxonMobil methanol-to-gasoline system, and acetogens for gas-to-liquid fuel fermentation. Similarly, companies like Velocys, Maverick, Fulcrum, and Enerkem have compared the cost of biogas to that of natural gas derived from fossil fuels and have opted to focus on the former. Enerkem, a Canadian company, has replaced fossil sources with waste to produce sustainable transportation fuels and chemicals used in everyday products [235]. Commercial-scale production of renewable methanol and ethanol is achieved by Enerkem from non-recyclable, non-compostable municipal solid waste. This innovative and environmentally friendly approach to waste management and energy diversification is based on eco-fuel feedstocks and aligns with the principles of the circular economy.

The production of ethanol involves the gasification of waste cellulose in multiple steps. First, methanol is synthesized from the produced synthesis gas, which is then converted to methyl acetate and acetic acid using rhodium-based catalysis. The acetic acid is esterified to obtain additional methyl acetate, and finally, all the methyl acetate is hydrogenated to produce ethanol. This multi-step technology can utilize both in situ-produced methanol and commercial methanol [235].

Asadullah et al. [236] emphasized the importance of efficient supply chain management, appropriate biomass pretreatment, and efficient fuel conversion in the development of biomass power generation. The authors investigated critical parameters for the generation of fuel gas with an optimal composition for turbines or internal combustion engines. These parameters include the type of gasifier (updraft, downdraft, fixed bed, fluidized

bed), gasifying agent (air, steam), temperature, pressure, and air/fuel ratio. For example, a fluidized bed gasifier allows for homogeneous heat distribution and fast heat transfer to the particles, resulting in improved reaction rates. However, it requires small biomass particles, leading to higher energy and economic costs. Similarly, a fixed bed gasifier (either updraft or downdraft) operates with high carbon conversion, longer residence time, and low gas velocity but is suitable only for small-scale power generation. Additionally, the product gas often contains impurities such as tar, particles, sulfur and nitrogen oxides, and ammonia, the quantities of which vary depending on the gas composition. Consequently, gas composition is crucial as internal combustion engines can only tolerate a limited concentration of contaminants, necessitating a purification process to minimize their presence. Physical filtration and catalytic hot-gas cleaning are the primary methods employed for purification. The primary approaches for electricity generation from the fuel gas obtained via biomass gasification include combined heat and power generation, fuel cells, and synthetic diesel production.

Gasification of lignocellulosic biomass offers several advantages, including high energy efficiency, flexibility in feedstock selection, and low greenhouse gas emissions [237,238]. The produced syngas can be utilized for various applications, such as electricity generation, heat production, and the synthesis of liquid fuels and chemicals [239]. Several factors influence the gasification process, including biomass composition, particle size, gasification temperature, residence time, and gasification agent [240,241]. To optimize gasification performance, research efforts have focused on improving reactor design, developing efficient catalysts, and exploring novel biomass pretreatment techniques [242–244]. Integration of gasification with other processes, such as gas cleaning and syngas upgrading, further enhances the overall efficiency and environmental sustainability of the biomass conversion process [245,246].

Pyrolysis of lignocellulosic biomass is a thermochemical process that offers an attractive route for the production of bio-oil, biochar, and syngas [247,248]. Bio-oil, also known as pyrolysis oil, is a complex mixture of oxygenated organic compounds that can be further refined into transportation fuels and chemicals [249–251]. Biochar, a solid residue obtained from pyrolysis, has applications in soil amendment and carbon sequestration [252]. Pyrolysis conditions, such as heating rate, temperature, and residence time, strongly influence product distribution and quality [253–255]. Various pyrolysis technologies, including fast pyrolysis, slow pyrolysis, and intermediate pyrolysis, have been developed to optimize bio-oil yields and properties [256–258]. Catalysts and additives are often employed to enhance the selectivity and quality of the bio-oil [259–261]. However, challenges such as the instability of bio-oil, high oxygen content, and the need for upgrading processes for bio-oil utilization remain areas of active research [262,263].

Recent advancements in gasification and pyrolysis technologies have focused on improving process efficiency, product quality, and environmental performance. Integrated gasification combined cycle (IGCC) systems have been developed to maximize energy conversion efficiency and minimize emissions by utilizing the syngas for power generation [264,265]. Co-gasification of biomass with coal or other carbonaceous materials has shown promise in improving the gasification process and diversifying feedstock options [266,267]. Moreover, the use of novel catalysts and catalytic gasification processes has demonstrated potential for enhancing gasification performance and syngas quality [268,269]. In the pyrolysis domain, the development of advanced reactors and integrated systems has aimed to increase bio-oil yields and reduce undesired by-products [270]. Upgrading techniques such as hydrodeoxygenation and catalytic cracking are being explored to improve the stability and quality of bio-oil for its utilization in transportation fuels [271–274].

In conclusion, gasification and pyrolysis of lignocellulosic biomass offer promising pathways to produce biofuels and bioenergy. These thermochemical conversion technologies provide opportunities for the efficient utilization of abundant biomass resources while reducing dependence on fossil fuels. Advancements in reactor design, biomass

pretreatment, catalyst development, and process integration have contributed to improving the efficiency, sustainability, and economic viability of these technologies. Continued research and development efforts are essential to overcome challenges and further optimize gasification and pyrolysis processes for large-scale implementation in the bioenergy sector.

2.7. Economic and Enviromental Consideration

The energetic valorization of lignocellulosic biomass presents a promising approach for sustainable energy production, with both economic and environmental considerations being crucial aspects to be addressed. Lignocellulosic biomass, including agricultural residues, forest waste, and energy crops, is a widely available and renewable resource that can be utilized for bioenergy production [62,275]. The economic viability of utilizing lignocellulosic biomass for energy generation relies on several factors, including feedstock availability, processing costs, energy conversion efficiency, and market demand for bioenergy products [157,276]. Additionally, the environmental impact associated with the energetic valorization of biomass needs to be carefully assessed to ensure a sustainable and low-carbon energy pathway.

Economically, the utilization of lignocellulosic biomass offers opportunities for rural development, job creation, and reduced dependence on fossil fuels [180,277]. Biomass is found worldwide but is not evenly distributed, tending to be concentrated in forests and rural areas. Furthermore, raw biomass, especially agricultural biomass, is humid and irregular in size, cannot be stored in its place of origin, and is very expensive to transport. For these reasons, challenges related to the logistics and supply chain management of biomass feedstock collection, transportation, and storage need to be addressed to ensure a reliable and cost-effective biomass supply [202,278]. Technological advancements in biomass pretreatment, enzymatic hydrolysis, fermentation, and thermochemical conversion processes have been crucial in improving the overall efficiency and cost-effectiveness of lignocellulosic biomass conversion [75,279,280]. Integration of bioenergy production with other industries, such as pulp and paper or bio-refineries, can lead to synergies and value chain optimization, enhancing the economic viability of biomass valorization [281,282].

Environmental considerations play a crucial role in the evaluation of the energetic valorization of lignocellulosic biomass. Biomass-derived energy has the potential to reduce greenhouse gas emissions compared to fossil fuels, contributing to climate change mitigation and improved air quality [8,283]. However, the overall environmental performance depends on factors such as biomass sourcing, production processes, and waste management strategies [180,283,284]. Sustainable sourcing of biomass feedstock, including responsible land use practices and biodiversity preservation, is essential to ensure that biomass utilization does not have adverse impacts on ecosystems [285,286]. The selection of conversion technologies that minimize emissions and waste generation, as well as the proper management of by-products and residues, are key considerations for environmental sustainability [283,287,288].

In their studies, Liu et al. developed a new framework to accurately assess the climate change impacts of biomass utilization. They found that second-generation biofuels, including biofuels derived from logging residues, wood, and wood waste, resulted in significantly reduced total greenhouse gas (GHG) emissions compared to fossil fuels. This reduction can amount to approximately 50% of CO_2 emissions compared to fossil fuels [289].

Hsu [290] investigated GHG emissions from biomass-based pyrolysis oil and demonstrated that greenhouse gas emissions could be reduced by approximately 50% when using pyrolyzed biofuels instead of fossil fuels.

According to Wang et al. (2020) [276] and Steele et al. [291], the global warming potential for pyrolysis bio-oil production is reported to be 30.85 kg CO_2 eq and 32 kg CO_2 eq, respectively. These findings confirm the promising potential for commercially converting biomass into fuels.

Life cycle assessment (LCA) is a valuable tool for assessing the environmental impact of lignocellulosic biomass utilization. LCA studies enable a comprehensive evaluation

of the entire life cycle, from biomass production and harvesting to energy conversion and end-use applications. They provide insights into environmental hotspots, resource consumption, emissions, and potential environmental trade-offs, allowing for informed decision-making and process optimization [292,293]. By considering the entire value chain and identifying opportunities for improvement, LCA studies contribute to the development of sustainable bioenergy systems that minimize environmental burdens [292–295].

To ensure the economic and environmental viability of the energetic valorization of lignocellulosic biomass, a holistic approach is required, integrating technological advancements, policy support, and stakeholder engagement. Research and development efforts should focus on improving biomass conversion technologies, optimizing process integration, and reducing costs via innovation and economies of scale [208,285,296,297]. Government policies and incentives that promote the utilization of biomass for energy purposes, such as feed-in tariffs and renewable energy targets, can stimulate investment and market development [203,298]. Collaboration between industry, academia, and policymakers is crucial to address technical, economic, and environmental challenges and foster the transition toward a sustainable bioenergy sector.

In conclusion, the energetic valorization of lignocellulosic biomass offers significant potential for sustainable energy production. Economic considerations, including feedstock availability and processing costs, must be carefully evaluated to ensure the viability of biomass conversion technologies. Environmental considerations, such as greenhouse gas emissions and resource utilization, should be addressed via responsible biomass sourcing, efficient conversion processes, and proper waste management. The integration of economic and environmental aspects, supported by technological advancements and policy frameworks, will pave the way for a sustainable and low-carbon bioenergy sector.

The LCA Approach for Bioenergy from Lignocellulosic Biomass

Life cycle assessment (LCA) studies focusing on bioenergy production from lignocellulosic biomass have provided valuable insights into the environmental impacts associated with different stages of the production process. These studies have identified specific impact categories that are significantly affected by the utilization of lignocellulosic biomass for bioenergy production. Among the impact categories commonly assessed, greenhouse gas emissions and fossil fuel depletion are often found to be substantially influenced by bioenergy production from lignocellulosic biomass [295,299]. This is primarily due to the displacement of fossil fuels with renewable biomass feedstock. For example, a study by Cherubini and Strømman (2011) evaluated the LCA of bioenergy production from lignocellulosic biomass and found that the substitution of fossil fuels with biomass feedstock led to a significant reduction in greenhouse gas emissions, contributing to climate change mitigation. Additionally, the study highlighted that the use of lignocellulosic biomass can reduce the depletion of fossil fuel resources, as the biomass feedstock is renewable and can be sustainably managed [300].

Other impact categories, such as eutrophication, acidification, and land use, also exhibit varying degrees of influence depending on the specific biomass utilization strategies and management practices employed. Guo, Song, and Buhain (2018) conducted an LCA of bioethanol production from corn stover and lignocellulosic biomass and found that the eutrophication potential was influenced by the agricultural practices associated with the production of the biomass feedstock. They noted that proper nutrient management and the adoption of sustainable agricultural practices can minimize eutrophication impacts [301].

Furthermore, the choice of land use for biomass cultivation and the potential impacts on biodiversity and ecosystem services have been highlighted in several studies [302,303]. Evaluating the environmental impacts of land use change and the preservation of natural habitats are crucial aspects in assessing the sustainability of lignocellulosic biomass utilization for bioenergy production [303,304].

Scientific studies have indicated that certain strategies for lignocellulosic biomass utilization are more viable and sustainable than others. Integrated biorefinery concepts, where

various products are derived from different components of the biomass, have been shown to maximize resource efficiency and reduce overall environmental impacts. Cherubini and Strømman (2011) highlighted the potential of integrated biorefineries in their study, which demonstrated the simultaneous production of biofuels, bio-based chemicals, and bio-based materials from lignocellulosic biomass. This approach maximizes the value extracted from the biomass feedstock and contributes to the development of a more sustainable bioeconomy [300].

Zhang et al. report the improvement in greenhouse gas emissions in the production of bioethanol from sweet potatoes. They also report that the next step on the road towards a totally sustainable bioethanol production is to improve energy efficiency and environmental benefits during the cultivation unit [305].

Furthermore, the utilization of agricultural residues and dedicated energy crops as feedstock for bioenergy production has demonstrated favorable sustainability characteristics. Song, Guo, and Zhang (2019) [306] conducted an LCA and techno-economic analysis of lignocellulosic ethanol production from corn stover and emphasized the advantages of utilizing agricultural residues as feedstock. They highlighted that agricultural residues, such as corn stover, leverage existing agricultural practices and avoid potential competition with food crops, making them a more sustainable feedstock option. Additionally, the study highlighted the importance of advanced conversion technologies, such as biochemical and thermochemical processes, in enhancing the efficiency and environmental performance of lignocellulosic biomass utilization for bioenergy production [306]. Similar results have been obtained by other scientists. Roy P.'s investigation showed that GHG emissions and the production cost of ethanol are dependent on feedstock, conversion technologies, system boundaries, allocation methods, and the utilization of byproducts. The LCA study also confirmed that both technological pathways are environmentally and economically viable. Although the results of this study indicate that similar benefits can be gained, they seem to be inclined toward the gasification-biosynthesis pathway. Biotechnological advances, especially in enzyme production, would improve the viability of the enzymatic hydrolysis process [307].

Gerrior et al., in their life cycle analysis, highlighted the importance of energy efficiency in bioethanol production and the recovery and exploitation of byproducts to make corn ethanol refineries economically sustainable and commercially competitive [308].

In conclusion, LCA studies provide valuable insights into the environmental impacts of bioenergy production from lignocellulosic biomass. Greenhouse gas emissions and fossil fuel depletion are major impact categories affected by the utilization of lignocellulosic biomass. Strategies such as integrated biorefineries, utilization of agricultural residues, and advanced conversion technologies have been shown to be more viable and sustainable. However, it is crucial to consider the specific context and local conditions when assessing the sustainability of lignocellulosic biomass utilization for bioenergy production.

3. High-Value-Added Products from Lignocellulosic Biomass

Apart from biofuels, lignocellulose is a great source of different high-value-added products [309]. The conversion of lignocellulosic wastes into value-added products enables the whole process to become more economically viable, according to biorefinery and circular economy concepts for sustainable development [310]. Chemical, physical, physico-chemical, biological, and enzymatic conversion can produce many bioproducts as carbohydrates, bioactive compounds, and lignin derivatives. Furthermore, the lignocellulosic biomass is an important substrate to produce several enzymes such as glycohydrolases (cellulases and hemicellulases) and oxidoreductases (laccase, peroxidases, and polysaccharide monooxygenases).

3.1. Platform Chemicals

The first possible chemicals from lignocellulose are C5 and C6 sugars, further convertible into a variety of platform chemicals [275], such as organic acids [311], succinic acid [312],

lactic acid [313], levulinic acid [314], fumaric acid [315], maleic acid [316], 2,5-furan dicarboxylic acid [317], 3-hydroxy propionic acid, aspartic acid, glucaric acid [318], glutamic acid (itaconic acid), furfural [319–322], hydroxymethylfurfural [323], 3-hydroxybutyrolactone, glycerol, sorbitol [324], and xylitol/arabitol [325,326]. These chemicals are, in turn, basic building blocks in chemical industries.

As an example, organic acids and their derivatives have a wide range of applications in several fields, such as food, animal feed, pharmaceuticals, cosmetics, plasticizers, textile products, coating materials, etc. Among them, succinic acid is a C4 dicarboxylic acid used in the pharmaceutical, agricultural, and food industries and is a precursor of adipic acid, 1,4-butanediol, methyl ethyl ketone, 1,3-butadiene, ethylene diamine disuccinate, 1,4-butanediol, γ-butyrolactone, tetrahydrofuran, succinic anhydride, fumaric acid and maleic acid [275,327,328]. Approximately 6.06 g/L of succinic acid could be synthetized by a Basfia succiniciproducens BPP7 strain, with a yield of 0.84 g/g and a productivity of 0.14 g/L/h. The following scale-up to 2.5 L gave the production of 9.4 g/L of succinic acid after 24 h under optimized fermentation conditions [329]. A high succinate concentration of 101 g/L was obtained from glucose by an Escherichia-coli-obtained batch and dual phase aeration fermentation system [330], as well as a high yield of 1.2 g/g and productivity of 1.31 g/L/h [331,332]. *E. coli* was also used to produce succinic acid from other substrates, such as corn stalk enzymatic hydrolysate with a concentration of 57.8 g/L, softwood hydrolysates with a concentration of 42.2 g/L [330], and cane molasses with a concentration of 26 g/L [333]. A high amount of the succinic acid concentration at 83 g/L and productivity of 10.4 g/L/h were obtained via Anaerobiospirillum succinoproducens [334]. Under optimized conditions, the yields of 134.25 g/L at the laboratory scale can be achieved [335]. Nevertheless, production costs and feasibility should be considered during succinic acid production on a large scale. Depending on raw material costs, product purity, productivity, yield, and recovery system, the cost of succinic acid production ranges from 5.9 to 9 $/kg, whereas its selling price is 2.26 $/kg or less [334].

Additionally, lactic acid is produced from the fermentation of carbohydrates and finds applications in food, pharmaceutical, personal care products, herbicides and pesticides, and textile and tanning industries. It can be converted into a variety of chemicals, such as lactate ester, lactide, acetaldehyde, 2,3-pentanedione, pyruvic acid, lactate, oxalic acid, propylene oxide, propanoic acid, and acrylates [227,336]. Typically, theoretical yields are 1 g/g or 2 mol/mol glucose using homofermentative lactic acid bacteria (*Lactobacillus acidophilus*, *L. amylophilus*, *L. bulgaricus*, *L. helveticus*, and *L. salivarius*), and 0.5 g/g or 1 mol/mol glucose via heterofermentative lactic acid bacteria (*L. brevis*, *L. fermentum*, *L. parabuchneri*, *L. reuteri*, *L. bifermentans*, *Leuconostoc lactis*, *L. sanfranciscensis*) [337]. The lag phase of the microorganisms is lower in fed-batch mode than in batch mode, with consequent improved lactic acid production. Indeed, lactic acid concentration increased from 40 g/L with batch SSF to 74.8 g/L with fed-batch SSF of corn stover using *L. pentosus* ([338]). Recombinant cellulolytic strategy in lactic acid bacteria significantly reduces lactic acid production costs, but it needs further research on genetic engineering. The food-grade lactic acid is sold at 1.38 $/kg (50% purity) and 1.54 $/kg (88% purity), while the technical-grade lactic acid costs 1.59 $/kg (88% purity). Therefore, the total production costs of lactic acid should be less than 0.8 $/kg, and the raw materials contribute to 40–70% of the total cost [337].

The removal of lignin is essential to enhance the yield and quality of fermentable sugars and platform chemicals. In a recent study, the highest degree of delignification (92%) was achieved via pre-treating lignocellulose with 8% of $NaClO_2$ [339]. However, several chemical, physical, physico-chemical, biological, and combined pretreatments were widely investigated to release the carbohydrate fractions of lignocellulosic biomass for enzymatic hydrolysis and subsequent bioconversion to value-added chemicals [340]. Novel catalytic pathways of lignocellulosic biomass to value-added chemicals were recently discussed [341–343]. Photocatalytic conversion of lignocellulosic biomass into platform compounds has attracted much recent attention [344,345].

The efficacy of acidic ionic liquids in the pretreatment and production of chemicals from lignocellulosic biomass has been investigated in many studies [346]. Corn straw, sorghum, and cellulose were converted into valuable chemicals (furfural, 5-hydroxymethylfurfural, levulinic acid) in ionic liquid–water media under different operational conditions. The highest performance (117.4 mg levulinic acid, 11.8 mg 5-hydroxymethylfurfural, and 9.4 mg furfural were obtained per g of sorghum) was achieved with 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4) at 180 °C after 30 min with a solvent ratio of 1:5 [347]. A novel process integrated lignocellulose pretreatment, fractionation, and conversion of hemicelluloses sugars into furfural, with the same biphasic solvent system (water/2-methyltetrahydrofuran) and phosphoric acid as recyclable catalyst [348]. Furfural was produced with yields of up to 57%, productivity of 5.7 g/L/h, and selectivity of up to 70%. The acid catalyst has the double function of lignocellulose fractionating and pentose dehydrating. Moreover, the biphasic system increases the overall selectivity of the process at high conversion rates and facilitates the in situ extraction of the produced furfural. Indeed, the use of the same catalyst-solvent system for both reaction steps simplifies the downstream processing. Therefore, the integrated process increases the overall efficiency of the fractionation, the delignification, the quality of lignin, and enzymatic hydrolysis rates after the pre-swelling step and avoids the addition of new chemicals in the second step.

3.2. Bioactive Compounds

Bioactive compounds are naturally present in fruit and vegetable biomass with beneficial effects on health. Carotenoids, flavonoids, and phenolics are some of these compounds. They can be extracted via solvent-based, solid–liquid, liquid–liquid, ultrasound-assisted, microwave-assisted, enzyme-assisted, and supercritical fluid extractions. Moreover, pharmaceutical, nutraceutical, and novel bioactive molecules can be synthesized from lignocellulosic residues, such as biologically active phenolic derivatives [349].

Polyphenolic compounds with bioactive functions were extracted from by-products of banana crops via a green process based on aqueous ethanol at optimized operational conditions. Ethanol concentration close to 50% and the highest tested temperature (78 °C) had the best performance with a total phenol content of 27.26 mg/g extract [350].

A sustainable process of extraction and separation of high-value phenolic compounds from wheat straw was developed. The first step was the biomass pretreatment and fractionation assisted by an ionic liquid. The phenolic extract was investigated by adsorption on specific polymeric resins. Finally, the supercritical CO_2 extraction was applied to further purify the phenolic fraction from the residual ionic liquid [351].

Various agro-industrial wastes from wineries, olive mills, and breweries were used to produce lignocellulolytic enzymes and extract antioxidant phenolic compounds by *Aspergillus niger* under solid-state fermentation, which increased the antioxidant activity (2.3-fold) after 1 day compared to the control [352]. The same strain was used for the solid-state fermentation of a mixture of grape pomace and wheat bran as carbon sources, followed by the recovery of the phenolic compounds [353].

Bioactive exo-polysaccharides were produced from a submerged culture of the white rot fungus *Inonotus* obliquus by lignocellulose decomposition of corn straw with a production of 1.38 g/L and a hydroxyl radical scavenging activity of 82.7% [354].

The microbial production of bioactive compounds from agricultural and forestry wastes has been demonstrated as technologically feasible and sustainable, as well as economically competitive. Lisin, an antimicrobial compound used for food preservation and biomedical applications, was produced via *Lactococcus lactis* from olive pruning and eucalyptus residues, together with lactic acid and other valuable products [355]. Ferulic acid was bio-produced via enzymatic hydrolysis of lignocellulosic cereal waste material and recovered via solid-phase extraction, compared with supercritical fluid extraction. Up to 3.69, 2,55, and 0.335 mg/g of ferulic acid was released after 48 h of enzymatic hydrolysis from rye bran with Viscozyme L., wheat with Viscoferm, and oat bran with Viscoferm, respectively. The supercritical fluid extraction with CO_2 and ethanol as a co-

solvent released up to 4.64 mg/g of ferulic acid from the bran matrix. The 10-fold and 30-fold scale-up experiments confirmed the applicability of enzymatic hydrolysis on an industrial scale, with the highest yield of ferulic acid obtained from rye bran after 48 h with Visco-zyme L [356].

3.3. Enzymes

Enzymes are natural proteins present in all living systems. They biocatalyze a wide range of reactions, but their high production costs still limit their application in industrial processes. Being rich in polysaccharides, lignocellulosic biomass is a source of lignocellulose-degrading enzymes via several microorganisms belonging to the fungi, yeast, bacteria, and actinomycetes categories. Fungi, particularly white rot fungi, have a strong ability to degrade lignocellulosic biomasses.

Two wood-degrading white rot fungi, *Obba rivulosa* and *Gelatoporia subvermispora*, produced lignocellulolytic enzymes from lignocellulose, and the total number of detected proteins was 947 and 845, respectively [357]. Among lignocellulosic biomass, food waste is a cheap raw material for the production of a variety of enzymes, such as amylase, β-glucanase, β-xylosidase, cellulase, inulinase, invertase, laccase, lipase, mannanase, pectinase, phytase, polygalacturonase, protease, transglutaminase, and xylanase [358].

Enzymes can be produced from food waste via lignocellulose pretreatment followed by enzymatic hydrolysis. The enzymatic hydrolysis is not necessary for some fungal organisms naturally growing on plant biomass, such as *Scytalidium thermophilum*, *Melanocarpus* sp., *Aspergillus* sp., and *Pleurotus* sp. [359].

Lignocellulosic biomass can be used as a substrate for enzyme production via microorganisms using different fermentation technologies, such as solid-state fermentation [360–362], submerged fermentation [363], sequential solid-state and submerged fermentation processes [364], and biomass pretreatment to obtain hydrolysates as substrates for enzyme production [364]. The solid-state fermentation mode is preferred over submerged fermentation mainly due to lower operational costs [362]. Solid-state fermentation is simpler than submerged fermentation for fungal laccase production from lignocellulosic agricultural wastes and has many advantages, such as higher productivity, higher efficiency, higher enzyme stability, lower production costs, and reduced environmental pollution. Laccase activity depends on white rot fungi and natural supports use, ranging from 1.65 U/g on prickly palm cactus husk via Rhizopus sp. to 535,000 U/g on wheat bran via Pseudolagarobasidium acacicola, from 180 U/L on corn silage via Trametes versicolor to 10,498 U/L on pine wood chips/orange peels via Trametes hirsuta [365]. The white rot fungus *Irpex lacteus* CD2 was used to degrade lignocellulose—with 63% of hemicellulose degraded after 15 days, 17.2% cellulose degraded after 10 days, and 80% acid-insoluble lignin degraded after 60 days and produced hydrolytic and oxidative enzymes via solid-state fermentation of corn stover. Total cellulase activity peaked at day 5 and remained at a high level from 40 to 60 days, while high hemicellulase activity appeared after 30 days. Instead, no ligninase activity was detected during the incipient stage of lignin removal, and only low lignin peroxidase activity was detected after 25 days [366]. A large amount of FPase (1.4 U/mL), CMCase (2.0 U/mL), cellobiohydrolase (0.6 U/mL), and β-glucosidase (2.7 U/mL) activities were produced on rice straw via Penicillium oxalicum GZ-2 in a 5 L bioreactor [337]. The on-site production of cellulase and hydrolysis of biomass is a promising strategy to reduce costs in ethanol production [367]. After the production step, the enzymes should be recovered and purified from the fermentation media. Because of low enzyme yield, concentration, and productivity, these downstream processes highly impact the overall production cost and strongly limit large-scale applications. Higher enzyme activity can be achieved via media optimization and genetically/metabolically modified enzyme-producing microbes. In addition, enzyme immobilization and purification in a single step make the enzyme recovery easier and less expensive [368].

3.4. Single Cell Protein (SCP)

Single-cell protein is one such value-added product that can be derived from various waste materials via microbial fermentation. Single-cell proteins (SCPs) or microbial biomass proteins are a kind of proteins extracted from single-cell micro-organisms such as algae, yeast, fungi, and bacteria, grown via fermentation on different carbon sources. Since 1968, when the term 'single cell protein' was coined [369], SCPs have been largely investigated.

In human nutrition, SCPs are used for vitamin transport, flavor enhancement, and as emulsifying agents, as well as in animal feed for poultry, pigs, calves, and fish [370]. SCPs have high nutritional value, not only for their prevalent protein content but also for the presence of amino acids, nucleic acids, minerals, enzymes, and vitamins [371]. Nevertheless, they are relatively cheap compared to other plant and animal sources because the waste substances used as raw materials are cheap, readily available, and eco-friendly [372]. Indeed, SCPs can be produced from waste lignocellulosic materials, properly pretreated to transform cellulose into fermentable sugars.

Among others, cactus pear biomass is a potential raw material in SCP production in arid and semi-arid regions [373].

The production of SCPs from lignocellulosic materials occurs in four steps: physical and chemical pretreatments, cellulase production, enzymatic hydrolysis, and assimilation or fermentation of cellulose and hemicellulose [374]. Therefore, lignocellulose acts as a substrate for the growth of micro-organisms cell mass via fermentation [375–377]. Submerged fermentation is the most used method for the production of SCP [378], but different fermentation systems were investigated in the literature.

One-stage and two-stage fermentations were compared in the production of SCPs from food waste via the yeast *Yarrowia lipolytica* [379]. Results showed that *Yarrowia lipolytica* could efficiently convert food waste to SCP, with a protein content of dry biomass of 24.2% *w*/*w* and 38.8% *w*/*w* via one-stage fermentation and two-stage fermentation, respectively.

Wheat bran—a lignocellulosic agricultural residue rich in carbohydrates—was solid-state fermented under optimized operational conditions with yeast *Candida utilis* and fungus *Rhizopus oligosporus* to produce SCPs. The maximum crude protein yield was 41.02% after a fermentation period of 48 h at 30 °C [380].

Upcraft et al. investigated the production of SCPs from the fungus Fusarium venenatum on fermentable sugars extracted from lignocellulosic waste using food-grade ionic liquids. This production of lignocellulosic mycoproteins resulted in technically feasible and environmentally sustainable but should be further explored before full commercialization [381].

Five fungal strains (*Trichoderma reesei*, *Fusarium venenatum*, *Fusarium graminearum*, *Thermomyces lanuginosus*, and *Aspergillus oryzae*) were evaluated for the production of SCPs from date residues after date syrup production. *A. oryzae* had the highest protein content (7.63%). The addition of nitrogen sources increased the protein content, with a maximum of 13.49% when 1% of ammonium sulfate was used [382].

Different lignocellulosic agricultural residues (rice straw, corncob, bagasse, and coffee hush) were compared for the production of SCPs by *Trichoderma reesei* in solid-state fermentation. In this case, the maximum crude SCP yield (22%) was obtained after 12 days at 30 °C with rice straw or coffee husk, combined with urea or NPK as sources of nitrogen at a C/N ratio of 20:1, with initial moisture of 75% and inoculum/substrate ratio of 1:1 *w*/*v* [383].

The yeast strain *Candida intermedia* FL023is another source of SCP from lignocellulosic hydrolysate and xylose with a crude protein content of 484.2 g/kg dry cell mass, a dry cell mass productivity of 0.86 g/L/h and a yield of 0.4 g/g sugar [384]. Pretrated and enzymatically hydrolyzed grass silage fiber was fermented with the filamentous fungus Paecilomyces variotii to efficiently produce SCPs [385].

Two lignocellulosic wastes, sugarcane bagasse and groundnut shells, were the substrates for the growth of Saccharomyces cerevisiae under solid-state fermentation. The production of SCP resulted in a maximum (4.65 mg/$g_{substrate}$) on groundnut shells [386].

Recently, microbial synthetic biology, genetic and genomic engineering, and biofoundry technologies have contributed to improving the productivity, nutritional, and functional quality of SCPs by engineering microorganisms [387].

However, SCPs for human consumption must be safe and undergo rigorous testing during the pre-marketing stage to remove possible toxic or carcinogenic compounds, heavy metals, and polycyclic hydrocarbons [369].

3.5. Antibiotics

With increasing global demands for antibiotics, lignocellulose can be considered a reliable raw material as a carbon source for microbial production as secondary metabolites [388]. The biosynthesis of antibiotics occurs under conditions of nutrient depletion when the specific growth rate of microorganisms becomes lower than a certain level [389]. Antibiotics were produced from readily available lignocellulosic agricultural residues using several microorganisms by both solid-state fermentation and submerged fermentation, but solid-state fermentation showed many advantages over submerged fermentation, such as low production cost and high productivity [390]. Cephalosporins are β-lactam antibiotics, and their fermentative production was widely investigated. Cephalosporin C was produced under solid-state fermentation by *Acremonium chrysogenum* ATCC 48272 from wheat bran, wheat rawa, rice bran, Bombay rawa, and barley. In this case, wheat rawa showed the highest antibiotic yield (22,281 μg/g) under optimized conditions of 1% *w*/*w* soluble starch and 1% *w*/*w* yeast extract as additives, an incubation period of 5 days, incubation temperature of 30 °C, a ratio of salt solution to wheat bran of 1.5:10 (*v*/*w*), inoculum level 10% *v*/*w*, moisture content of solid substrate 80% and pH 6.5 [391]. Cephalosporin C was also produced by *Tolypocladium* sp. from wheat bran, with a yield of 16 ± 8 mg/100 g of bran cooked with distilled water and 114 ± 20 mg(100 g of wheat bran hydrolyzed with 0.2 N HCl [392]; and by *Cephalosporium* sp. NCIM 1039 from wheat bran, wheat grains, rice grains, barley, and rice bran, with wheat bran showing the best results (750 U/g) with potato starch 1% *w*/*w* and urea 1% *w*/*w* as additives, incubation period of 7 days, incubation temperature at 30 degrees C, inoculum level 10% *w*/*v*, moisture content of solid substrate 80% and pH 7.0 [393].

Other esamples of antibiotics produced from lignocellulosic biomass under solid-state fermentation were cephamycin C by *Streptomyces clavuligerus* NT4 (21.68 ± 0.76 mg/$g_{\text{dried substrate}}$) [394] or Nocardia lactamdurans NRRL 3802 (15.75 ± 0.27 mg/$g_{\text{dried substrate}}$) [395] from agricultural wates (wheat bran, soy flakes, soy flour, soy grit, tamarind seed powder, rice stock, cotton hull, wheat rawa, rice bran, saw dust, and amaranth stack waste); haloduracin by *Bacillus halodurans* from wheat bran (3000 AU/$g_{\text{dry substrate}}$) [396]; mevastin by Penicillium citrinum NCIM 768 from wheat bran (0.0554 g/L) [397]; neomycin by Streptomyces fradiae 2418 from solid agro-industrial residues such as apple pomace, cotton seed meal, soy bean powder, and wheat bran, with apple pomace showing the highest antibiotic production (2765 μg/$g_{\text{substrate}}$) [398]; rifamycin B by *Amycolatopsis mediterranei* MTCC 14 from coconut oil cake, groundnut oil cake, ground nut shell and rice husk, with coconut oil cake and ground nut shell showing higher antibiotic yield than groundnut oil cake and rice husk (1.32–1.46 mg/$g_{\text{dried substrate}}$) [399]; tetracycline by different *Streptomyces* strains from agricultural wastes including groundnut shells, corncob, corn pomace and cassava peels, with the Streptomyces sp. OXCq gives the highest tetracycline production (13.18 mg/g) on peanut shells as substrate in solid fermentation [400], and oxytetracycline by Streptomyces spp. on groundnut shells, corncob, corn pomace, and cassava peels, with Streptomyces vendagensis ATCC 25507 producing 120 mg/g of oxytetracycline on groundnut shells [401].

3.6. Biostimulants

Biostimulants or metabolism inducers are compounds, microorganisms, or other materials that can stimulate plant growth and development when used in small quantities in the soil or applied directly onto the leaf surface [402]. They are an emerging class of agricultural inputs in a fast-growing market. Microbial biostimulants include rhizobacteria

and arbuscular mycorrhizal fungi, which promote plant growth [403]. Nevertheless, the recovery of biostimulant compounds from crop residues is gaining much attention and is still being investigated.

Humic-like substances obtained isolated by alkaline oxidative hydrolysis from lignin-rich agro-industrial residues showed biostimulant activity toward maize germination and early growth [404].

A promising biostimulant, feed nutrient, and photodynamic drug is 5-aminolevulinic acid. It can be bioproduced from glucose as the main carbon source, and its production cost decrease if cheap biomass is used. Agricultural residues, such as molasses, cassava bagasse, and woody biomass, can replace refined sugars. As an example, 5-aminolevulinic acid was effectively produced with a titer of 18.5 g/L from cassava bagasse by metabolically *engineered Corynebacterium glutamicum* in a one-step fermentation process [405]. Indole-3-acetic acid is another biostimulant produced from lignocellulosic wastes by *Trichoderma harzianum* under solid-state fermentation (101.46 $\mu g/g_{dry\ matter}$) [406].

3.7. Economic and Environmental Consideration

Large-scale production of high-added value compounds is capital-intensive, and much of the annual operating cost is attributed to plant equipment, installation, and raw materials. Lignocellulosic wastes are the cheapest and most abundant sources of carbohydrates, and their valorization makes the process cost-effective and efficient. Solid-state fermentation is preferred over the submerged fermentation method in maintaining a low cost of production. Nevertheless, the industrial biocatalytic conversion of lignocellulose needs to address further aspects.

Firstly, the biocatalysts have to be improved in order to achieve higher yields and productivity. Indeed, biocatalytic processes are still rarely applied at the industrial scale since the single conversion steps (pretreatment, hydrolysis, and fermentation) may exhibit low conversion rates, low efficiencies, or high costs. Low yield, low titer, and low productivity are all mainly due to technical problems, including the inability to control the C/N ratio, low sugar concentration, diauxic growth caused by C5 and C6 sugars, and the presence of microbial inhibitors produced from lignin breakdown [358].

Moreover, the product recovery and the recycling of water and biocatalysts should be considered. Finally, the evaluation and model-based synthesis of the complete process chain needs to be performed since all steps are strongly associated and need to be harmonized.

Therefore, although the current yields of high-value-added products at the experimental scale are high under proper conditions, it is still difficult to culture microorganisms in an anaerobic environment at a commercial scale. For this reason, production costs and feasibility should be considered during large-scale production, requiring further improvements such as metabolic pathway modulation, fermentation process optimization, culture media optimization, and genetic engineering techniques.

The feasibility of the bioprocess has been evaluated by several techno-economic analyses. Modeling results demonstrate that lignocellulose-derived high-added-value com-pounds could be produced at a competitive price [407], but further techno-economic assessment in scaled-up processes should be addressed, taking into account the green concepts of circular economy and biorefinery.

From the environmental point of view, platform chemicals from waste lignocellulosic biomasses are cost-competitive with petroleum-derived alternatives [408]. Since the conventional use of chemicals and catalysts produces environmentally hazardous and corrosive solid and liquid wastes, industries are interested in biological, non-catalytical, and energy-efficient processes. As an example, AVA Biochem developed a fully water-based pilot-scale process for the conversion of sugars into the bio-based 5-HMF [409].

Although lignocellulose-derived proteins are more expensive than meat proteins, they could be potentially more sustainable for human consumption because their decarbonization contributes and minimum arable land usage being agricultural residues, with no competition with the food chain.

4. Biopolymers

Pesticides, heavy metals, and dyes are among the most harmful materials in nature. They can be present at various concentrations in the environment, for example, in water, soil, and the atmosphere. The accumulation of these pollutants, over time, has caused various harmful effects on man, including congenital malformations, mental disorders, genetic mutations, and a reduced level of oxygen in the environment; hence, there is strong interest in eliminating these toxic substances [410].

The development of new technologies aimed at eliminating these pollutants is necessary, although the removal of excess heavy metals from the environment to achieve an acceptable level of quality is still a major challenge.

Biopolymers, polymeric materials produced by organisms, represent a promising alternative and an advantageous choice, arousing much interest in the entire community [411]. They have become increasingly popular as they are associated with a long list of benefits. The main one is that no fossil resource is used for their production but only biomass, contributing to the reduction in environmental pollution at sea and on land by reducing, for example, carbon dioxide emissions. Furthermore, natural polymers are also employed as a sustainable solution for the improvement in soil mechanical properties, such as soil strength, thus increasing the productivity of grain crops [412].

They are valid natural substitutes for chemical and synthetic polymers and are entirely bio-based, produced by living organisms. Biopolymers are mainly available as polymer units and monomer units joined together via a covalent bond to form long chains, which can be defined as linear, branched, or crosslinked [413].

They constitute a large family of materials, are biodegradable, recyclable, decomposable in the environment, and based on their numerous sources, can be classified into three main groups (Figure 2) [414].

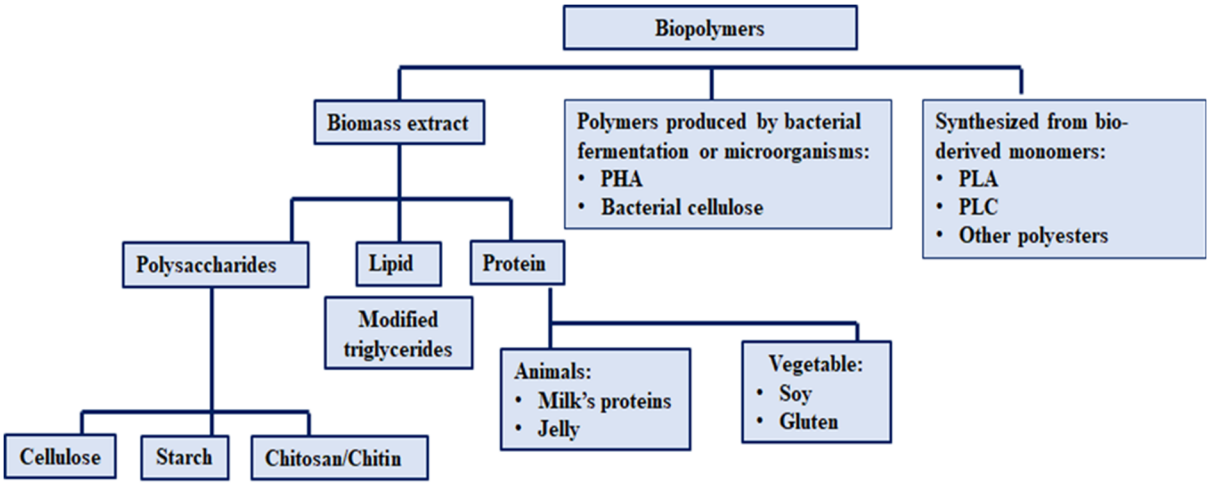

Figure 2. Classification of the main biopolymers [414].

Some of the more common biopolymers are chitosan, starch, and cellulose. They are the most essential and abundant polymers in nature. Thanks to their ability to be easily handled, their versatility, and their sustainability, they are used in various fields, such as film production and pharmaceutical and medical applications [415].

In this context, the attention paid to biopolymers from lignocellulosic biomass has significantly increased. Lignocellulose biomass mainly consists of cellulose and hemicellulose, two complex carbohydrate polymers, plus lignin, a phenolic polymer. It is the most abundant fraction of biomass of vegetable origin in nature, with different application possibilities, allowing, for example, the replacement of many traditional plastics [43,416] or by biosorbents for the removal of toxic pollutants from wastewater [417].

The advantages of using biopolymers are innumerable. The analysis of the biopolymer markets, particularly aimed at lignocellulose, starch, and chitosan, has shown that

these products have the greatest potential for development towards a more sustainable environment. However, experimental procedures in practical applications are still limited to a laboratory scale.

4.1. Biodegradable Plastics

The accumulation of petrochemical plastic materials, despite being among the most useful and comfortable materials for daily life, has caused serious problems to the habitat of fauna and flora, also posing a threat to humans [418]. Most plastics take hundreds of years to degrade, and for this reason, one-third of plastic ends up as marine or land pollution [419,420].

Just think that every year, millions of tons of plastic waste end up in the oceans. This waste decomposes, giving life to "microplastics". Several studies have shown that microplastics will inevitably be ingested by plankton. The latter represents the basis of the oceanic food chain, and it also provides the most important mechanism for absorbing carbon in the atmosphere. The presence of microplastics affects the ability of the oceans to absorb carbon, with disastrous climatic consequences [421].

In a society that is increasingly careful about the issue of pollution, it is necessary to find an alternative that has a lower impact on the ecosystem. The demand for economic and ecological materials increases to reduce waste management, and the interest of the industrial world in biodegradable plastics is also growing considerably. To mitigate environmental damage, the concept of "circular economy" was born, and biodegradable plastics have been proposed as a potential solution for creating a more sustainable world.

Although the words "bioplastic" and "biodegradable" are often mistakenly used interchangeably, they are not synonymous (Table 4).

Table 4. The most important terms and their definition.

Terms	Definition
Bioplastics	Biodegradable plastics or plastics that are produced from renewable materials or biological raw materials.
Bio-based plastics	Plastics full or partially derived from renewable carbon sources.
Bio-compatible	Materials classified as non-toxic for living organisms.
Biodegradable	Microorganisms can divide materials into polymeric or monomeric components, such as biomass, water, methane, and carbon dioxide. Compostable, biodegradable materials can be entirely converted into benign rubbish in a few months.
Compostable	Compostable materials can be decomposed using controlled biological processes with microorganism-based standard mixtures.
Marine-degradable	Fossil fuels or bio-based plastics can be degraded into water and carbon dioxide in the marine environment by light and heat catalyzed.
Non-toxic/Toxic	Materials containing residual components and degradation products that are non-toxic or toxic to living organisms, respectively.
Plastics	Polymeric materials with synthetic or quasi-synthetic derivation.
Renewable source	The matter that can be used and replaced incessantly, i.e., biomass.

A biodegradable product is defined in this way when it can degrade naturally, thanks to the enzymatic action of microorganisms such as fungi and bacteria. This mechanism, activated automatically, ends without the help of man and avoids contamination of the surrounding environment. Biodegradable plastics can originate from renewable sources (e.g., vegetable or animal origin) or from fossils (e.g., oil) [422]. Bioplastics, instead, are made using resources that do not originate from fossil fuels, with the advantage of being obtainable from a renewable source, generally linked to the use of plants as raw material, such as biomass.

The use of alternative materials to improve or replace the classic plastic materials deriving from petroleum resources is growing rapidly. The use of new products and biopolymers has, in fact, become a consolidated practice thanks to their technical feasibility, abundance, easy availability, and convenient characteristics.

Furthermore, the use of composite blends of different polymers with other natural additives, such as corn starch, silica, or lignocellulose, can improve and refine the property characteristics of bioplastic materials. Among them, lignocellulosic raw materials are the most abundant and inedible biomass.

The enormous annual amount of lignocellulosic waste is in the order of 140 Gt (gigaton tons) and can present the major pollutant of the environment and cause many diseases if not managed correctly. However, this resource represents potential wealth for the replacement of plastics and fossil-based materials [423,424].

The characteristics of the final product are determined both by the intrinsic properties of the ingredients of the blend and by the morphology of the blend. Common configurations might include double emulsion, drip and double emulsion, and continuous and laminar structures. Improving the derived properties of the structural changes could result in better strength, better toughness, and high electrical conductivity [425,426].

The formation of intermediate morphologies is influenced by the processing method, the ratio of the composite biopolymers, and their viscoelastic characteristics. Furthermore, the uniformity and distribution of the polymers are a function of their viscosity ratio, the interfacial tension, the addition of a third stabilizing phase, and, finally, the type of process and its parameters [427].

Although biodegradable plastics are associated with adjectives such as "green" and "eco-friendly" and promise to reduce the problems of climate change and waste, the transition from conventional to ecological plastics still represents a difficult challenge today. However, it is expected that the continued development of new and advanced technologies will facilitate the creation of sustainable "green" processes for the production of biodegradable plastics [359].

4.2. Biocomposites and Bio-Fibers Production

In recent decades, the interest in environmental protection has led researchers to focus on bio-composites and biofibers as valid alternatives to synthetic materials [428].

Natural fibers can be classified into two main groups (Figure 3): vegetable and animal fibers, according to the source of extraction [429,430].

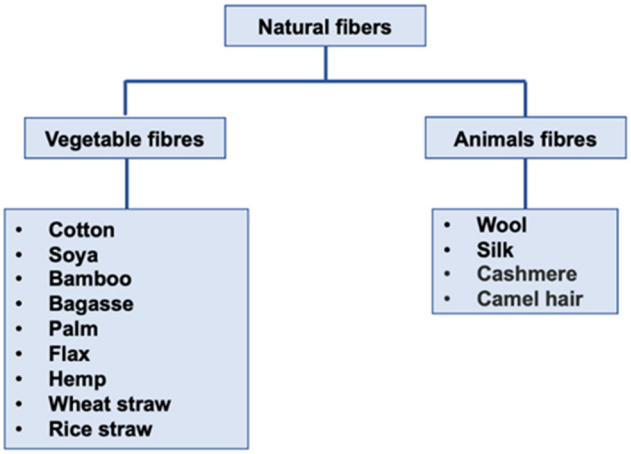

Figure 3. Classification of biofibers.

Vegetable fibers are mainly made up of cellulose, hemicellulose, and lignin. Animal fibers are mainly classified into two types: hair and secretions [428].

Composite materials reinforced with biofibers have proved to be the most promising materials of the last period thanks to their resistance, bending stiffness [431], biodegradability, and thermal stability [432].

In particular, lignocellulosic fibers are among the most important natural bio-resources in the world. They are widely used as reinforcement in bioplastics, replacing them with

synthetic fibers [433]. They are widely available; moreover, they have a low density, low cost, and excellent mechanical properties.

Along with several benefits, there are some drawbacks associated with these lignocellulosic fibers. Several studies, in fact, discuss the compatibility between lignocellulosic fibers and other biopolymers due to improper bonding to the composite, leading to poor performance. Another important limit is related to the hydrophilic properties of biofibers. They tend to swell with moisture absorption, causing serious damage to the matrix when made as a composite [428]. Despite this, many advances are underway to improve these precious natural resources.

5. Current State of Technologies: Industrial Scale-Up and Commercial Prospects

The scale-up process for the valorization of lignocellulosic waste is underway, with continuous efforts to optimize and improve the efficiency of conversion technologies on larger scales. While significant progress has been made, several challenges and limitations need to be addressed to achieve widespread commercial implementation.

In the field of biochemical conversion, expansion efforts have focused on improving the efficiency of enzymatic hydrolysis and fermentation processes. Optimization of enzymatic cocktails, development of robust and high-performance enzymes, and advancements in fermentation technologies have contributed to improved conversion yields [150,151,434,435]. Furthermore, process integration and optimization, including the utilization of co-products and waste streams, have been crucial in enhancing the economic feasibility of commercial-scale bioethanol production from lignocellulosic biomass [436–438].

Thermochemical conversion technologies have also undergone scale-up processes. Pyrolysis and gasification systems have been enhanced to handle larger quantities of feedstock and improve product yield and quality. Ongoing research aims to improve process stability, increase overall efficiency, and develop advanced reactor designs [176,260,439]. Integration with other industrial processes, such as combined heat and power (CHP) systems, is being studied to enhance the overall energy efficiency of lignocellulosic waste conversion [139,440,441].

The scale-up process for the production of chemical and bio-based materials from lignocellulosic waste is still in its early stages. Research and development efforts are focused on improving yield, selectivity, and cost-effectiveness of conversion pathways. Integrated biorefinery concepts are being explored, aiming at maximizing the utilization of all biomass components, including cellulose, hemicellulose, and lignin, to improve process efficiency and economic feasibility [442–444].

Despite the progress made, challenges such as feedstock variability, logistics, high capital costs, and market demand uncertainties continue to hinder the scaling-up process. Techno-economic assessments and life cycle analyses are underway to evaluate the feasibility and sustainability of lignocellulosic waste valorization on a commercial scale [300,445,446].

In conclusion, the scale-up process for the valorization of lignocellulosic waste is ongoing, with advancements in biochemical and thermochemical conversion technologies. Efforts are focused on optimizing conversion processes, improving efficiency, and addressing economic and sustainability challenges. Continuous research and development, along with supportive policies and market incentives, are crucial to promote the widespread adoption of lignocellulosic waste valorization technologies.

5.1. Commercial-Scale Operating Technologies

The commercial-scale valorization of lignocellulosic waste has gained significant momentum in recent years. Several technologies have been successfully applied for the conversion of lignocellulosic biomass into value-added products, indicating promising commercial potential.

An important technology is the biochemical conversion process, particularly enzymatic hydrolysis and fermentation, which enables the production of bioethanol from lignocel-

lulosic feedstocks. Numerous commercial-scale bioethanol plants have been established worldwide, utilizing lignocellulosic biomass such as agricultural residues, dedicated energy crops, and forest residues [447–450]. For example, the "Project Liberty" facility in the United States, operated by POET-DSM, is one of the largest commercial-scale cellulosic bioethanol plants, converting corn stover into bioethanol [451]. In Europe, Clariant's fully functional Sunliquid cellulosic ethanol facility in Podari, Romania, with an investment of $120 million, has been in full operation since October 2021. Clariant employs enzymatic degradation to break down straw cellulose into sugars, followed by yeast fermentation to transform these sugars into ethanol. With an annual production capacity of 50,000 metric tons (t) of ethanol, sourced from approximately 250,000 tons of locally available straw and other agricultural remnants, the plant has successfully secured long-term sales agreements with Shell for its entire output [452]. In Italy, Versalis, Eni's chemical company, announced in February 2022 that it has started the production of bioethanol from lignocellulosic biomass at Crescentino (Vercelli). The plant is capable of processing 200,000 tons of biomass per year, with a maximum production capacity of approximately 25,000 tons of bioethanol per year [453].

Thermochemical conversion processes, such as pyrolysis and gasification, have also demonstrated commercial feasibility for the valorization of lignocellulosic waste. Pyrolysis technology has been used in commercial-scale facilities to produce bio-oil, biochar, and syngas from various lignocellulosic feedstocks [176,454]. Gasification processes have been employed for syngas production, which can be further converted into biofuels, chemicals, and heat [232,455]. Several gasification plants, such as the GoBiGas plant in Sweden, have been established to convert lignocellulosic biomass into synthetic natural gas (SNG) [456].

This is a completely mature technology, and in fact, it is now possible to find gasification systems on the market that work using lignocellulosic biomass as feedstock for the production of syngas, biochar, and heat energy [457,458].

Furthermore, lignocellulosic waste has been utilized as a feedstock to produce bio-based chemicals and materials. Commercial-scale facilities have been established to produce platform chemicals, such as levulinic acid, furfural, and lignin-based chemicals, which can be further utilized for the synthesis of various value-added products [434,459]. Additionally, lignocellulosic biomass has been employed in the production of bio-based polymers, bio-based composites, and bio-based plastics, with some companies already commercializing these products [460–464].

In summary, several technologies for the valorization of lignocellulosic waste have achieved commercial-scale implementation. Biochemical conversion processes for bioethanol production, thermochemical processes such as pyrolysis and gasification, and the production of bio-based chemicals and materials demonstrate the commercial feasibility of lignocellulosic waste valorization.

5.2. The Second-Generation Biorefineries Prospective

Biorefineries utilize biomass in complex processing systems to produce a diverse range of fuels, chemicals, and bio-based materials [465]. Second-generation biorefineries show promise for sustainable energy and chemical production by utilizing feedstocks such as lignocellulosic materials, non-edible crops, and various waste streams, including black liquor, sawdust, bark, and straw. In contrast to first-generation biorefineries, these advanced facilities employ more sophisticated processes that result in higher-value products. However, there are several technical and economic challenges, such as the high costs of these processes and operational considerations, that must be overcome to ensure the success of second-generation biorefineries [281,466,467].

The integration of different biorefineries plays a crucial role in maximizing the utilization of feedstocks, generating a maximum yield of value-added products, and minimizing waste by converting it into lower-value products. This approach enhances output and reduces overall costs [465]. For instance, the decline in paper demand has led to a trend of converting pulp mills into integrated biorefineries within the wood industry. In this

context, lignin is recovered from black liquor and used by pulp mills for wood or paper processing [468]. In 2012, the European Union (EU) introduced a bioeconomy strategy with the primary objective of developing sustainable biorefineries that efficiently convert cost-effective lignocellulosic materials into bioenergy and bioproducts [469]. The EU aims to derive 25% of transportation energy from biofuels produced in biorefineries by 2030 [470]. Numerous European and international scientists are actively researching ways to reduce the cost of these processes [446,471–476].

The integration of biorefineries is critical for the cost-effective and sustainable conversion of lignocellulosic biomass into value-added products, as it addresses challenges related to low efficiency, high operational costs, and significant energy consumption in various biomass conversion processes. However, there are several limitations that hinder the applicability of this approach at a commercial scale. These challenges include high capital costs, biorefineries being limited to specific biomass types or products, an inconsistent biomass supply chain, and unique bottlenecks associated with each conversion process, making scaling up more difficult [281,477–479].

6. Conclusions

In conclusion, this study focused on the valorization of lignocellulosic agricultural waste to produce valuable products. The findings presented here highlight the immense potential of utilizing agricultural waste as a sustainable and renewable resource for the generation of various valuable products.

Using a combination of innovative processes and technologies, the conversion of lignocellulosic agricultural waste into biofuels, biochemicals, and biocomposites has been demonstrated. The utilization of waste biomass not only reduces the environmental burden associated with waste disposal but also offers a viable solution for reducing dependence on fossil fuels and mitigating greenhouse gas emissions.

The analysis of different agricultural waste streams revealed their rich composition in terms of cellulose, hemicellulose, and lignin content. These components serve as valuable feedstocks for the production of biofuels, such as ethanol and bio-oil, which can be employed as alternative energy sources. Furthermore, the extraction and transformation of lignocellulosic components into platform chemicals, such as furfural, levulinic acid, and hydroxymethylfurfural, offer great potential for the synthesis of various high-value biochemicals.

Several conversion pathways were explored, including physical, chemical, and biological processes. Physical pretreatment methods, such as milling and steam explosion, proved effective in enhancing the accessibility of cellulose and hemicellulose for subsequent enzymatic hydrolysis. Chemical pretreatment, such as acid or alkaline treatment, facilitated the breakdown of lignin and improved the overall digestibility of the biomass. Biological processes, such as enzymatic hydrolysis and fermentation, were successfully employed to convert the released sugars into biofuels and biochemicals.

The utilization of lignocellulosic agricultural waste for the production of biocomposites was also investigated. By incorporating the waste biomass as a reinforcing filler in polymer matrices, biocomposites with enhanced mechanical properties and reduced environmental impact were fabricated. These lignocellulosic-based biocomposites exhibit promising potential in various applications, including packaging materials, construction panels, and automotive components.

Moreover, the economic feasibility and environmental sustainability of lignocellulosic waste valorization were assessed. Techno-economic analysis revealed that the production of biofuels and biochemicals from agricultural waste could be economically viable, especially when coupled with appropriate government policies and incentives. Life cycle assessment studies demonstrated the environmental benefits of utilizing agricultural waste, including reduced carbon emissions, decreased energy consumption, and lower ecological footprint compared to traditional fossil fuel-based processes.

Overall, this study underscores the significance of lignocellulosic agricultural waste as a valuable resource for the production of biofuels, biochemicals, and biocomposites. The findings presented here contribute to the growing body of knowledge on sustainable waste management and the development of a circular bioeconomy. The successful valorization of agricultural waste not only offers economic opportunities but also contributes to mitigating climate change and promoting environmental stewardship.

Further research and development efforts are warranted to optimize the conversion processes, enhance product yields and quality, and scale up the production of valuable products from lignocellulosic agricultural waste. Collaboration between academia, industry, and policymakers is crucial for addressing the technical, economic, and regulatory challenges associated with large-scale implementation. By harnessing the untapped potential of lignocellulosic agricultural waste, we can create a more sustainable and resource-efficient future, promoting the transition towards a circular bioeconomy.

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