Review

Agricultural Wastes and Their By-Products for the Energy Market

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Abstract: The conversion of lignocellulosic agricultural waste into biofuels and other economically valuable compounds can reduce dependence on fossil fuels, reduce harmful gas emissions, support the sustainability of natural resources, including water, and minimize the amount of waste in landfills, thus reducing environmental degradation. In this paper, the conversion of agricultural wastes into biomethane, biohydrogen, biodiesel, bioethanol, biobutanol, and bio-oil is reviewed, with special emphasis on primary and secondary agricultural residues as substrates. Some novel approaches are mentioned that offer opportunities to increase the efficiency of waste valorization, e.g., hybrid systems. In addition to physical, chemical, and biological pretreatment of waste, some combined methods to mitigate the negative effects of various recalcitrant compounds on waste processing (alkali-assisted thermal pretreatment, thermal hydrolysis pretreatment, and alkali pretreatment combined with bioaugmentation) are evaluated. In addition, the production of volatile fatty acids, polyhydroxyalkanoates, biochar, hydrochar, cellulosic nanomaterials, and selected platform chemicals from lignocellulosic waste is described. Finally, the potential uses of biofuels and other recovered products are discussed.

Keywords: lignocellulosic waste; biofuel; platform chemicals; pretreatment

1. Introduction

The remains of processing agricultural products that are not food are defined as agricultural waste. This waste is generally classified into crop residues (husk, leaves, straws, bagasse from harvesting rice, wheat, sugarcane, corn, other crops, fruit peels, vegetable trimmings, damaged or rejected products such as, e.g., leftover feed, plant debris), animal residues (animal excreta, bedding materials), waste generated from distribution of fruits and vegetables, processing of agricultural products or managing livestock (fertilizer cans, packaging materials), and hazardous waste (insecticides, pesticides) [1–3].

The agriculture sector is one of the biggest producers of waste [4]. The yearly production of agricultural waste is estimated to be about 998 million tons, of which organic waste accounts for 80% [2]. Agricultural waste is a major source of lignocellulosic components, which are primarily composed of 30–50% hemicellulose, 30–40% cellulose and 8–21% lignin [3,5]. Moreover, agricultural waste is a source of valuable compounds, such as proteins (also enzymes), fatty acids, dietary fibers, flavors, and bioactive compounds, which can be applied in the food, pharmaceutical, and cosmetic industries.

Residuals of wheat, corn, rice, sugarcane, and sugar beet are the main agricultural materials used in biofuel production. Their compositions are 19–24% lignin, 27–32% hemicelluloses, 32–44% cellulose, and 4.5–9.0% ashes (sugarcane bagasse); 5–24% lignin, 19–27% hemicelluloses, 32–47% cellulose, and 19% ashes (rice straw); 15–20% lignin, 20–25% hemicellulose, and 33–40% cellulose (wheat straw); $11.9 \pm 2.3\%$ lignin, $44.4 \pm 5.2\%$ hemicellulose, and $38.8 \pm 2.5\%$ cellulose (corn cob); and 1–2% lignin, 25–36% hemicellulose, and 20–25% cellulose (sugar beet pulp) [6–8].

Apart from the need to properly manage agricultural waste to mitigate its adverse environmental impact and health risks, valorization of this waste to recover additional

value is crucial, particularly because this waste is produced in huge amounts and constitutes a significant portion of the total waste matter generated in developed countries. Even though agricultural waste and its by-products contain valuable components, its economic value may be lower than the cost of collecting, transporting, or processing the waste. Therefore, to completely utilize this waste as part of a biorefinery approach and to avoid the unintentional loss of high-value products, it is important to search for a wide range of marketable compounds in waste materials and their components.

Among renewable resources, biofuels and bioproducts represent a compelling way to reduce dependence on fossil fuels, minimize greenhouse gas emissions, and promote the principles of the circular economy [9]. Anaerobic digestion (AD) and other biomass conversion technologies are at the forefront of this transition, transforming organic waste materials into valuable resources [10]. These processes not only provide pathways for the production of biofuels but also pave the way for the production of a variety of bioproducts. In general, lignocellulose biomass can be used in biochemical and thermochemical conversion pathways as a feedstock for the generation of second-generation biofuels (bioethanol, biobutanol, biomethane, biohydrogen, and biodiesel), which can serve as fossil fuel alternatives [3]. According to the European Biogas Association (EBA) [11], biomethane production in Europe was almost 20% higher in 2022 than in 2021. In Europe, in 2022, the production of biogases (biogas and biomethane combined) amounted to 21 bcm. The production of biomethane alone increased from 3.5 bcm in 2021 to 4.2 bcm in 2022. As a result of biofuel production, 31 Mt (dry matter (d.m.)) of digestate was produced in 2022, which could cover 15% of the EU's nitrogen-based demand for fertilizers.

In addition to biofuel production, agricultural waste can be used to synthesize chemicals and polymers. In particular, each of the components of lignocellulosic matter can be utilized for value-added products [4]. Hemicellulose and cellulose can be hydrolyzed to glucose and other monomeric sugars, which can serve as carbon sources for microbial fermentation. Lignin can also be used to produce various chemicals with industrial importance, such as phenols, vanillin, keto acids, aromatic diacids, quinones, cyclohexanes, and olefins [12], or as a source of thermal energy [13]. In addition, agricultural waste can be transformed into carbon nanostructures [14] or used for the production of construction materials, such as bricks [15].

Agricultural waste is a source of secondary metabolites that have antioxidant and anti-inflammatory properties. These bioactive compounds, including polyphenols, can be recovered [16] and used as new raw materials in the pharmaceuticals, cosmeceuticals, and nutraceuticals industry, and in food and feed production; as such, they can be considered value-added products [17].

Intensified valorization methods can turn the waste into sustainable bioproducts, which include energy, fertilizers, platform chemicals, and other valuable products. As feedstock accounts for 75% of the total cost of biofuel production [18], the valorization of agricultural waste could help to significantly reduce the costs of this process. AD has been considered the most mature and efficient technology for transforming waste residues into various bio-based products. In general, primary agricultural residues (such as straws, sugarcane tops) are less used for energy production than secondary residues (bagasse, husks) because primary residues are used as fertilizers or animal feed [19]. During the early development of biofuel production technologies, different food crops served as fermentation substrates. However, taking into account competition with humans for food, waste biomass has predominated in feedstocks in recent years. This paper provides an overview of the production and utilization of biofuels, such as biogas/biomethane, biohydrogen, bioethanol, biodiesel, bio-oil, and biobutanol, as well as some platform chemicals and other products of various agricultural residues. This paper outlines strategies for intensifying production of these substances through different methods of waste pretreatment.

This paper introduces novel approaches to the valorization of lignocellulosic agricultural waste, emphasizing the conversion into biofuels and a broad spectrum of economically valuable compounds through innovative hybrid systems and combined pretreatment

methods. It explores advanced technologies such as microbial fuel cells for bioelectricity generation and the production of diverse products including volatile fatty acids, polyhydroxyalkanoates, biochar, and nanomaterials. The study's novelty also lies in its holistic analysis of the environmental benefits and economic implications, showcasing the potential of agricultural waste as a sustainable resource for energy and material production, thereby addressing key sustainability challenges in the energy sector.

2. Production of Biofuels—Overview of Substrates from Agriculture

Biofuels include gaseous biofuels (biogas, biomethane, biohydrogen) and liquid biofuels (biodiesel, bioethanol, bio-oil, biobutanol). As they provide energy obtained from biomass and biomass products, they are considered sustainable alternatives to conventional fuel [20,21].

In biochemical processes employing microorganisms and enzymes, biomass components are broken down into precursors like amino acids, fatty acids, and sugar, which are converted into biogas/biomethane/biohydrogen through AD by anaerobic sludge, bioethanol by fermentation of starch, butanol and methanol by distillation of dry woods, and biodiesel and oil by transesterification of fatty acids. To intensify these processes, newer co-culturing techniques are used for the production of biodiesel, bioethanol, and biobutanol. This approach both minimizes environmental concerns and maximizes the net profits of valorizing agricultural waste for biofuel production because the waste is cheap, biodegradable, and widely available [22].

2.1. Production of Biogas

After the microbial hydrolysis of complex carbohydrates into simple sugars, fermentation of sugars into organic acids, and subsequent methanogenesis to convert them into CH_4 and CO_2, the biogas that is produced can be used as a renewable substitute for natural gas, powering homes, industry and even vehicles [23]. Biogas usually consists of CH_4 (55–65%) and CO_2 (35–45%), along with N_2 (0–3%), H_2 (0–1%), and H_2S (0–1%) [24]. The digestate (AD residues) can be utilized as a nutrient-rich fertilizer, thus closing the loop in a circular bioeconomy. Biogas with a CH_4 content of more than 50% can be produced from such wastes as sunflower husks, maize waste, soybean straw, wheat straw, rice straw, rice husks, mix cereal grains, vegetable residuals, carrot leaves, potato peels, grape seeds, apple pomace, grape vinasse, glycerine, molasses, palm oil cake, sugarcane waste, etc. (Table 1).

To intensify the production of biogas and decrease its cost, the application of an external current or electric potential in microbial electrolysis cells has been employed. Electroactive microorganisms, which are attached to the anode, oxidize organic matter to CO_2 by using the electrode material as the final electron acceptor. As an electron acceptor, graphite is usually used. The electrons produced are used to catalyze the generation of reduced target molecules such as H_2, CH_3COOH, or CH_4 [1]. When the system is operated for electromethanogenesis catalyzed by electroactive microorganisms attached to the cathode, the oxidation of organic matter on the anode can be combined with biomethane production (biomethane is biogas that contains almost 100% CH_4).

During conversion of hemicellulose-rich biomass under anaerobic conditions, furfural is produced. In concentrations of 100–500 mg/L, furfural inhibited CH_4 production; however, a concentration of 1000 g/L stimulated methanation [25]. The products of further conversion of furfural are chemicals, fuel additives, and alternative fuels that are desired by the economy [26], e.g., coffee crop waste has been valorized to use its C5 fraction to produce biogas and furfural; in addition, variants with and without ethanol production from the remaining C6 fraction have been explored [27]. Yields of 0.34 g furfural/g xylose and 81.1 mL CH_4/gram VSs (volatile solids) were obtained from the hydrolysate fraction. After acid pretreatment, the solid fraction was used to produce ethanol, and 0.47 g ethanol/g glucose was produced. However, as economic prefeasibility was achieved at the base scale when processing for furfural and at a higher scale when processing for biogas, this combined biorefinery approach was not considered an effective option.

For biogas production, mono-digestion of some agricultural waste is not recommended due to its high carbon content, which leads to an excessively high C/N ratio. To increase yields, co-digestion has been employed by co-feeding lignocellulosic biomass with other organic substrates, such as food waste or animal manure [25]. Examples of co-digestion strategies to enhance biogas yields, involving blends of different biomass types, include the mixing of agricultural solid wastes with cow dung [28]. The highest production of CH_4 (297.99 NL/kg VS) was achieved at the ratio of these substrates of 60:40 (wt). On the other hand, mixing agricultural wastes with sewage sludge resulted in a decrease in CH4 production from 284 mL CH_4/g VS (proportion 100:0) to 176 mL CH_4/g VS (proportion 0:100) [29]. Similarly, agricultural waste increased the CH_4 yield from chicken manure by 93% [30].

Table 1. Production of biofuels from various substrates.

Type of Waste	Yield	References
Methane production		
Sunflower husks	147 L CH_4/kg VS	[31]
Maize waste	338 L CH_4/kg VS	[32]
Soybean straw	196 L CH_4/kg VS	[33]
Wheat straw	290 L CH_4/kg VS	[32]
Rice straw	302 L CH_4/kg VS	[32]
Rice husks	300 L CH_4/kg VS	[34]
Mix cereal grains	345 L CH_4/kg VS	[33]
Residual cabbage and cauliflower (1:1, *w/w*)	250 L CH_4/kg VS	[35]
Carrot leaves	312 L CH_4/kg VS	[36]
Potato peels	446 L CH_4/kg VS	[36]
Grape seeds	71.4 L CH_4/kg VS	[33]
Apple pomace	204 L CH_4/kg VS	[37]
Grape vinasse	274 L CH_4/kg VS	[33]
Glycerine	241 L CH_4/kg VS	[31]
Molasses	456 L CH_4/kg VS	[33]
Palm oil cake	402 L CH_4/kg VS	[38]
Sugarcane waste	278 L CH_4/kg VS	[32]
Hydrogen production in photofermentation		
Potato starch powder	77.78 mL/(L·h)	[39]
Shrub landscaping waste	73.82 ± 0.06 mL/g TS	[40]
Corn stover	74.58 mL/g TS	[41]
Corncob	84.7 mL/g TS	[42]
Hydrogen production in dark fermentation		
Potato waste	27.5 mL/g VSS	[43]
Wheat straw	31.67 mL/g VSS	[43]
Cotton stalk hydrolysate	179 mL/g VSS	[44]
Raw cassava starch	240 mL/g VSS	[45]
Bioethanol production		
Wheat straw	250–300 L/Mg d.m.	[46,47]
Rice straw	250–280 L/Mg d.m.	[48,49]
Sugarcane straw	250–450 L/Mg d.m.	[50,51]
Potato waste	21.7 g/L	[52]
Sunflower stalk	80–150 L/Mg d.m.	[53,54]
Maize stover	250–350 L/Mg d.m.	[47,55]
Sugarcane bagasse	0.29 ± 0.02 g ethanol/gglucose and xylose	[56]
Biodiesel production		
Corn stover	2.2 g/g	[57]
Cassava starch	0.187 g/g	[58]
Rice bran oil	94.12%	[59]

VS—volatile solids, TS—total solids, VSS—volatile suspended solids, d.m.—dry matter.

In addition, the AD of lignocellulosic agricultural waste is limited by the recalcitrant components of the waste; pretreatment methods to enhance microbial growth and improve the rate of biogas production are discussed in Section 4.

Biogas upgrading is a crucial process in the valorization of biogas from AD. This process significantly improves the quality of the biogas by removing impurities and increasing the CH_4 content, making it comparable to natural gas in terms of energy content and usability [9]. The upgrading of biogas involves crucial steps such as the removal of CO_2 to enhance CH_4 concentration and calorific value, elimination of contaminants like H_2S, NH_3, and water vapor that can corrode equipment and diminish biogas efficiency, and the compression and storage of biomethane for various applications [60].

A variety of technologies are employed in biogas upgrading, each selected based on its advantages and the specific requirements of the operation. These include water scrubbing, which uses high-pressure water to absorb CO_2 and H_2S and is favored for its simplicity [61]; chemical scrubbing, which uses chemicals like amines for selective absorption of impurities [62]; pressure swing adsorption, utilizing adsorbent materials for impurity binding [63]; membrane separation, which relies on semi-permeable membranes for selective gas permeation [64]; and cryogenic separation, distinguishing gases based on condensation temperatures at very low temperatures, noted for its high efficiency in CH_4 purity but also its energy intensity [65].

The advantages of biogas upgrading extend to all ecological and economic areas. It offers a renewable, carbon-neutral alternative to natural gas, reduces greenhouse gas emissions, and promotes new markets and employment opportunities in the green energy sector [66]. Upgraded biogas or biomethane has a wide range of applications, from feeding into gas grids to providing clean fuel for vehicles and meeting the energy needs of industry and households, underlining its versatility as a renewable energy source.

Despite its advantages, biogas upgrading faces challenges, such as the high costs associated with some technologies and the need for efficient gas purification methods to meet stringent quality standards [67]. Addressing these challenges through continuous research and development is critical to reducing costs, improving efficiency, and expanding the applications of upgraded biogas to ensure its role in a sustainable energy system.

Biogas is a versatile energy source. The direct use of biogas is mainly as a fuel for cooking and heating in households, especially in developing regions [68]. Biogas is also used to generate electricity through combustion engines and combined heat and power (CHP) systems [69]. These systems exploit the energy content of biogas to produce electricity and heat, showcasing biogas as an efficient fuel for power generation with the potential to significantly contribute to the renewable energy mix. The indirect use of biogas covers a wider range of applications and focuses on the conversion and upgrading of biogas into more versatile forms such as biomethane and bio-CO_2. Upgraded biogas, especially biomethane, can be used as a vehicle fuel or injected into the natural gas grid, expanding its utility for transportation and as a substitute for conventional natural gas. In addition, bio-CO_2, a by-product of biogas upgrading, is identified as a valuable feedstock for chemical production, underlining the circular economy potential of upgrading biogas.

2.2. Production of Biohydrogen

Although biohydrogen production is considered a clean technology, creating a biofuel with a high energy content and good energy balance (due to its high heat of combustion of 142.9 kJ/g and a thermal efficiency that is 30–60% higher than that of traditional fossil fuels) when utilizing agricultural waste, low productivity is the main limitation of this approach [70]. The potential of biohydrogen was found to be highest for untreated rice straw (58,002 Mm^3/year) followed by that of untreated wheat straw (34,680 Mm^3/year) [71].

In the biochemical pathways of H_2 production from lignocellulosic biomass, H_2-producing microorganisms transform organic matter into H_2 by means of light fermentation (photofermentation), dark fermentation, or photo-dark fermentation.

In photofermentation, photosynthetic bacteria (with the most studied being *Rhodopseudomonas palustris*, *R. faecalis*, *R. capsulata*, *Rhodospirillum rubrum*, and *Rhodobacter sphaeroides*) degrade low-molecular-weight organic substrates and simultaneously produce H_2 in the presence of light and anaerobic conditions [70]. These bacteria cannot directly use macromolecular organic compounds that are difficult to hydrolyze. Instead, they use carbohydrates, such as glucose and other easily hydrolyzed compounds, and various low-molecular-weight organic acids. Examples of H_2 yields in photofermentation of selected agricultural wastes are given in Table 1.

In dark fermentation, H_2-producing microorganisms convert organic compounds into low-molecular-weight metabolites under anaerobic conditions with no external input of light, and they simultaneously produce H_2. The most studied microorganisms include obligate anaerobic bacteria (*Caldicellulosiruptor saccharolyticus*, Ruminococcus, and Rumen bacteria) and facultative anaerobic bacteria (Enterobacter and *Escherichia coli*) [70]. Employing mixed populations of H_2-producing microorganisms is more advantageous than using mono-populations, which are less likely to adapt and use complex organic compounds. The yields of H_2 in dark fermentation with different agricultural wastes are listed in Table 1. Due to faster production of H_2, the ability to operate without light, and better adaptability to substrates, dark fermentation for H_2 production is more suitable for the industrial scale. However, industrial production is restricted by the low yield of the process (4 mol H_2/mol glucose), which in practice is usually even lower.

In combined photo- and dark fermentation, the substrate is first subjected to dark fermentation to produce biohydrogen, and then liquid metabolites are further converted into biohydrogen in the next step (photofermentation), thus improving H_2 yield [70]. Alternatively, both functional groups of bacteria are co-cultivated, and dark fermentation and photofermentation occur in the same reactor as one-step dark-photofermentation. Enhancing H_2 production in combined processes was achieved, for example, using a mixture of fruit and vegetable waste and cheese whey powder [72]. In the dark stage, low H_2 production resulted from the metabolism directed to lactate production. In the overall process, the highest H_2 potential rate of 157.5 mL H_2/(L·h) was observed at the C/N ratio of 39 in the dark stage and at a dilution of its effluent of 1:2.

To enhance the activity of enzymes and promote the growth of key microorganisms, a combination of mixed organic substrates or mixed microbial cultures has been explored. For example, agricultural waste was co-digested with sewage sludge [73,74]. The mixture of carbon-rich rice straw and nitrogen-rich sewage sludge resulted in a H_2 yield of 0.74 mmol H_2/g VS of straw and a stable and high H_2 content of 58% [74].

In addition to the use of biochemical methods to produce H_2, thermochemical processes (gasification and pyrolysis) have also been employed [25,75]. In gasification, lignocellulosic biomass is heated in the presence of oxygen or steam transformed into a mixture of H_2, CO, and other gases. The produced syngas can be further converted to extract H_2 or utilized to synthesize liquid hydrocarbon fuels. In pyrolysis, lignocellulosic biomass is thermally decomposed in the absence of oxygen. The resulting bio-oil can be upgraded to obtain liquid hydrocarbon fuels and H_2-rich gas. In thermochemical processes, agricultural crop wastes such as rice husk, straw, corncob, sugarcane bagasse, sunflower bagasse, etc., were used [75,76].

2.3. Production of Bioethanol

Lignocellulosic biomass is biochemically converted to bioethanol by pretreatment to release hemicellulose and cellulose before hydrolysis, followed by hydrolysis of cellulose into glucose and hemicellulose into pentoses and hexoses, and then fermentation of reducing sugars into ethanol. H_2, methanol, and succinic acid are also produced [77]. Fermentation techniques include simultaneous saccharification and fermentation, and separate hydrolysis and fermentation [78]. The yields of ethanol are higher in simultaneous processes. Subsequent distillation concentrates the ethanol to the desired purity level for fuel use [79].

Production of bioethanol can be conducted by transforming a wide range of carbohydrate-rich agricultural lignocellulosic waste. Second-generation bioethanol is produced from non-food plants and residual materials, including agricultural waste (molasses, bagasse, and other carbohydrate-rich residuals of corn, wheat, barley, switchgrass, sugarcane, sugar beet, potatoes, etc.), municipal waste, food waste, and wood processing residues [25]. Wheat straw, which is the second most abundant lignocellulosic material in the world, is an important source of cellulose for ethanol production [22].

For example, acid hydrolysis plus enzymatic saccharification of sugarcane bagasse, sugarcane bark, cornstalk, corncob, or cornhusk, followed by fermentation at 30 °C for 72 h with *Saccharomyces cerevisiae*, resulted in maximum ethanol yields of 6.72, 6.23, 6.17, 4.17, and 3.45%, respectively [80]. Other bioethanol yields from various substrates are shown in Table 1.

Bioethanol is widely used as a fuel for transportation [81]. It can be blended with gasoline to reduce carbon emissions and increase the octane rating of the fuel. Blends of up to 10% ethanol (E10) are common in many countries and can be used in conventional gasoline vehicles. Higher blends such as E85 (85% ethanol) require flexible fuel vehicles designed to run on different ethanol concentrations [82]. The utilization of bioethanol in energy generation primarily revolves around its use in fuel cells and as a renewable source for heat and electricity production. Bioethanol's high-octane rating and clean-burning properties make it an attractive option for replacing or supplementing traditional fossil fuels in various energy generation applications [83]. Bioethanol can be converted into H_2 through steam reforming, which then feeds into fuel cells to produce electricity [84]. This process is particularly appealing for its high efficiency and the potential for low emissions, depending on the source of heat for the reforming process. The adaptability of bioethanol fuel cells makes them suitable for a range of applications, from providing power in remote locations to serving as backup power sources in critical infrastructure [85]. In combined CHP plants, electricity and heat energy are generated simultaneously by burning bioethanol. This dual power approach improves the overall efficiency of the system by utilizing the heat that would otherwise be wasted when generating electricity alone [86]. Combined heat and power systems that run on bioethanol can significantly reduce the operating costs and carbon footprint of industrial plants, commercial buildings, and residential complexes. The solvent properties of bioethanol make it valuable for the production of paints, varnishes, and lacquers [87]. It is also used in pharmaceuticals, cosmetics and personal care products, where its volatility and ability to dissolve a wide range of substances are highly valued [88]. The use of bioethanol as a solvent supports the shift towards safer, more environmentally friendly chemical processes and products. Bioethanol is a key ingredient in the synthesis of ethylene and other basic chemicals that serve as building blocks for plastics, rubber, and synthetic fibers [89]. The transition to bioethanol-derived ethylene is particularly significant in the context of reducing the chemical industry's carbon footprint and dependence on oil and gas feedstocks. Innovations in biotechnology and materials science have also enabled the use of bioethanol in producing biodegradable plastics and other biomaterials [90]. These applications not only contribute to reducing plastic pollution but also highlight the versatility and sustainability of bioethanol as a feedstock.

2.4. Production of Biodiesel

Biodiesel (an alkyl ester of fatty acids), which is receiving much recognition as a replacement for conventional fuels, is produced when plant oils are trans-esterified with an alcohol (ethanol, methanol, or other) in the presence of a catalyst (e.g., metal oxides) [91]. Enzymatic hydrolysis of cellulose and hemicellulose into fermentable monomeric sugars is a key step of the process. The fermentation of released sugars proceeds via yeast (*Saccharomyces cerevisiae*) fermentation, in which the ethanol produced is subsequently transformed into biodiesel via transesterification reactions [92]. Alternatively, direct production of biodiesel from lignocellulosic sugars via fermentation by bacteria and Archaea has been explored [93,94].

Biodiesel can be produced from several plant oils (soybean, rapeseed, and canola), waste cooking oils, non-edible oils, food residues, residual biomass, etc. [95] (Table 1).

Catalysts improve alcohol solubility, thus increasing the reaction rates of biodiesel synthesis. Agricultural wastes may be sources of cost-effective, easily available, easy-to-produce, and environmentally friendly catalysts, which can offer a good alternative to commercial catalysts. One source of sustainable and environmentally friendly catalysts that increase the cost-effectiveness of biodiesel synthesis is rice husk or coconut husk; products of burning this are used to make reactive silica, which acts as a catalyst [2,91].

Glycerol, which is a waste material from the biodiesel industry, can be transformed into value-added products, such as succinic acid, citric acid, poly(3-hydroxybutyrate), and 1,3-propanediol, as well as some intermediates used for microbial production of polymers [96]. Glycerol has found several applications in the cosmetics and pharmaceutical industries [96]. In addition, waste glycerol can serve as an external organic carbon source in wastewater treatment plants, which improves the efficiency of nitrogen and phosphorus removal from organic-poor wastewater [97].

Biodiesel serves as a renewable, biodegradable, and cleaner-burning alternative to conventional diesel fuel [98]. It can be used in diesel engines without major modifications, either in the pure form (B100) or as an admixture to mineral diesel in various concentrations. The use of biodiesel can significantly reduce emissions of particulate matter, carbon monoxide, hydrocarbons, and sulfur oxides, thus helping to improve air quality and public health [99]. Biodiesel is also utilized in diesel generators for electricity production, especially in remote or off-grid locations, as a sustainable alternative to diesel fuel [100]. It can be used in standalone power generators or as part of hybrid systems combined with renewable energy sources like solar or wind power [101]. This application is particularly beneficial for reducing carbon emissions and improving energy security in regions without access to the electricity grid. In regions where heating oil is a common fuel for space heating, biodiesel blends can be used as a direct substitute [102]. This application is becoming increasingly popular in private and commercial heating systems, as biodiesel has a lower CO_2 footprint than conventional heating oils. It can be used as a solvent or cleaning agent. This benefits industries that want to reduce their environmental impact and improve worker safety by replacing more toxic chemicals. Biodiesel and its by-products are valuable raw materials in green chemistry for the manufacture of a wide range of products, including biodegradable lubricants, cosmetics, pharmaceuticals, and plastics [103]. This utilization not only adds value to the biodiesel production chain but also aligns with the principles of the circular economy and sustainability.

2.5. Production of Biobutanol

Biobutanol can be produced via a two-step fermentation process known as acetone–butanol–ethanol (ABE) fermentation, performed mainly by clostridial species. First, lignocellulosic biomass is pretreated and enzymatically hydrolyzed. Subsequently, releasing sugars are fermented via solvent-producing microorganisms to yield biobutanol. As a result of genetic modifications of microorganisms to increase the biobutanol production rate, Moradi et al. achieved a yield of 112 g biobutanol/kilogram of alkali-/acid-pretreated rice straw [104].

The technology for cellulosic alcohol production can be classified into four major variants: (1) separate hydrolysis and fermentation (SHF), (2) simultaneous saccharification and fermentation (SSF), (3) simultaneous saccharification and co-fermentation (SSCF), and (4) consolidated bioprocessing (CBP). Currently, the SHF and SSF processes are the most frequently applied [105].

As promising feedstocks for biobutanol production, agricultural residues, energy crops, and forestry waste have been used. For example, rice straw and sugarcane bagasse were alkaline pretreated and then enzymatically hydrolyzed [105]. For the inoculum, an efficient butanol-producing bacterium was obtained from H_2-producing sewage sludge. Biobutanol was produced via either separate hydrolysis and fermentation (SHF) or a com-

bination of SHF with simultaneous saccharification and fermentation (SHF-SSF). With SHF of bagasse, the maximum butanol concentration, productivity, yield, and ABE ratio were 2.29 g/L, 1.00 g/L·d, 0.52 mol butanol/mol reducing sugar, and 0.12:1:0.06, respectively, whereas with rice straw, they were 2.92 g/L, 1.41 g/L·d, 0.51 mol butanol/mol reducing sugar, and 0.19:1:0.1, respectively. After SHF-SSF of bagasse, the maximum butanol concentration, productivity, and yield were 1.95 g/L, 0.61 g/L·d, and 0.37 mol butanol/mol reducing sugar, respectively, whereas after SHF-SSF of rice straw, they were 2.93 g/L, 0.86 g/L·d, and 0.49 mol butanol/mol reducing sugar, respectively. Independently of the fermentation type, rice straw was a more efficient feedstock than bagasse. H_2 formation occurred simultaneously (3.2–4.4 L/L and 1.8–2.2 mol H_2/mol reducing sugar) during ABE fermentation.

More economically viable production of energy can be achieved through the integrated use of lignocellulosic biomass for the production of biobutanol and biogas. Residual sugars and lignin as by-products of biobutanol fermentation can be utilized as substrates for biogas production via AD [106]. This can increase overall energy efficiency.

Biobutanol can be used as a fuel for internal combustion engines and as a transport fuel. It has also found applications in diverse industrial sectors including chemical intermediates, paints/coatings, cosmetics, pharmaceutics, herbicides, and detergent formulations. Moreover, it is used as resins or plasticizers [107].

2.6. Production of Bio-Oil

Bio-oil (pyrolysis oil) is a complex mixture of oxygenated organics that can be further converted into transportation fuels. To convert agricultural waste into liquid hydrocarbons such as bio-oil, thermochemical technologies such as intermediate pyrolysis [108], fast pyrolysis, hydrothermal liquefaction [49], or gasification with Fischer–Tropsch synthesis [109] have been used.

Pyrolysis may result in converting about 40–75% of biomass (on a dry basis) into pyrolytic oil, 10–20% into biochar, and the rest into synthetic gas [110]. However, in practice, the bio-oil yields are lower. For example, when treating rice straw at 300–450 °C, 34.5 wt% was maximally achieved at 400 °C [111]. The growth of temperature from 300 to 450 °C decreased the yield of solid residue and increased the yield of gas. Bio-oil contained mostly phenol, 2-ethyl-phenol, 2-methyl-phenol, 2-methoxy-phenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxy-phenol.

More effective systems of microwave-assisted pyrolysis were developed. Temperature growth from 400 to 600 °C increased the yields of bio-oil (31.9 wt%) from rice straw and decreased the yields of bio-oil (27.45 wt%) from *C. oleifera* shell [112]. However, bio-oil produced from the shell had higher contents of phenols, aldehydes, and alcohols. When supporting microwave-assisted co-pyrolysis of corn stover and scum with catalysts such as CaO and HZSM-5 zeolite, the maximum yield of bio-oil was obtained at 550 °C [113]. Higher bio-oil yields (up to 42.1 wt%) were obtained from corn cob [114]. The addition of $MgCl_2$ as a catalyst did not improve the bio-oil yield. The higher heating value of corn cob-based bio-oil (22.38 MJ/kg) than that based on corn stover, saw dust and rice straw resulted from the predominance of ethyl ether and 2-bromo-butane.

Thermocatalytic reforming is an emerging technology that proceeds in two main steps: (i) the intermediate pyrolysis step, in which thermal heating and decomposition of the biomass occur in the absence of oxygen, and (ii) the reforming step, in which catalytic cracking of vapors occurs at elevated temperatures to promote the synthesis of gas formation and the evaporation of organic matter. The condensation yields deoxygenated bio-oils with fuel properties [115]. The possible energy, mass, and carbon efficiencies can reach 40%, 20%, and 32%, respectively [109].

Bio-oil tends to have low pH values (2–3) and consists of water and oxygenated aliphatic and aromatic chemicals, including esters, alcohols, ketones, aldehydes, phenols, furans, and sugars. Such a rich composition of bio-oils results from the pyrolysis of cellulose, hemicellulose, and lignin. As a result, bio-oils can be co-fed with fossil fuels or

used directly in boilers [114]. They can be used for H_2 production or converted into car fuel by hydrodeoxygenation. In addition, bio-oils serve as a source of various chemicals such as phenols, biodiesel, polyurethane, or monomers for plastic production [116].

2.7. Hybrid Technologies

In biofuel production technology, the use of two-phase AD has been explored, in which a fermentation step with H_2 production is followed by methanation, resulting in biogas enriched with up to 10–20% H_2 [1]. This technology increases conversion yields by up to 37% [117] and leads to the production of bio-hythane (hydrogen-enriched methane), reducing NO_x and GHG emissions [118]. Bio-hythane can be used in conventional natural gas vehicles. The following substrates were used for this purpose: wheat straw, rice husk, sugarcane bagasse, and mixed fruit and vegetable waste, and the percentages of bio-hythane produced were 29.75%, 16.74%, 53.64%, 43.54%, and 40.92%, respectively [119].

2.8. Production of Bioelectricity by Microbial Fuel Cells (MFCs)

MFCs are used to transform organic substances from complex waste compounds into electrical energy using microbial activity. In MFCs, microorganisms oxidize organic matter, resulting in the production of electrons that are transferred by various enzymes within some cells. Finally, these electrons are released at the cathode to reduce oxygen [120]. Since microorganisms cannot degrade the agricultural waste in MFCs directly to produce electricity, acidic or enzymatic pretreatment is required to produce fermentable sugar hydrolysates [120].

Agricultural wastes used for bioelectricity generation include wheat and rice straw, cassava mill effluents, corn stover, plant and flower wastes, vegetable wastes, etc. Examples of MFC performance are 93.97 mW/m^2 (corn stover, [121]), 660 mW/m^2 (corn straw, [122]), 190 mW/m^2 (rice straw, [123]), and 230 mW/m^2 (corn cob pellets, [124]).

2.9. Production Costs of Energy Sources

The estimated costs associated with the production of different energy sources are given in Table 2. For example, on the European market, in 2022, the cost of biomethane production was 80 EUR/MWh, comprising 16 EUR/MWh (raw material), 32 EUR/MWh (CAPEX), and 32 EUR/MWh (OPEX) [125]. However, it should be considered that the costs depend on the availability of wastes in a local market, regional agricultural conditions, costs of feedstock, kind of feedstock and its form (raw waste or silage), the local retail prices, local policy scenario, production scale, available technologies, type of pretreatment, methods or substrates that, for example, increase the available sugars, biogas upgrading, and optimization of the fermentation process including the application of genetic engineering of microorganisms or the use of enzymes [126–132].

Table 2. Production costs of the energy sources.

Biofuel	Production Costs	References
Biogas	0.05–0.18 USD/kWh	[129]
Biomethane	0.54–0.78 EUR/m^3	[133]
Biohydrogen	10–20 USD/GJ	[134]
Bioethanol	1310 USD/m^3	[126]
Biodiesel	760–1120 USD/m^3	[130]
Bio-oil	17–24 USD/GJ	[135]
Biobutanol	500–800 USD/m^3	[131,132]

3. Production of Other Value-Added Products

In addition to the much-discussed biofuels such as biogas, biodiesel, and bioethanol, a number of other valuable bioproducts are obtained from the conversion of biomass. These products offer sustainable alternatives to their conventional counterparts, further enhancing the environmental and economic benefits of biomass use.

3.1. Production of Volatile Fatty Acids (VFAs) and Polyhydroxyalkanoates (PHAs)

Some biological mechanisms, including dark fermentation, photofermentation, and two-stage AD, employ microorganisms to generate VFA-rich residual effluents from hydrolysis of lignocellulose [136,137]. VFAs serve as starting materials for further conversion into PHAs and derivatives. These valuable bio-based compounds can be used as biopolymers.

In 2023, the international market for PHAs was estimated at 4.8% of total bioplastic production (105,000 tons), and this is expected to increase to 13.5% by 2028 [138]. PHAs have a high potential in waste valorization, as the flexible acidogenic fermentation of largely heterogenic wastes delivers a stable substrate for PHA production; the wide range of PHA properties lead to the use of this polymer as a component of various bioplastics; the production process takes place under mild conditions; and no excess sludge is produced (the PHAs account to 70% of the biomass) [1].

Fed-batch fermentation has been researched for PHA production from agricultural waste [139]. The hydrolysate after enzymatic saccharification of lignocellulosic biomass contains hexose and pentose sugars. For PHA production, microorganisms that have a high capacity to ferment such sugars are commonly used. These can be fast-growing, ethanol-producing bacteria (e.g., *Zymomonas mobilis* and *Saccharomyces cerevisiae*), as they can absorb a lot of sugar.

The production costs of PHAs must be minimized to be competitive with conventional plastics. In the aerobic production of these biopolymers, usually in a phosphate-limited process, only about 50% of the main carbon sources end up in the final products [140]. Therefore, there is a need for cheap carbon sources and also for cheap complex nitrogen sources. These can be sourced from agricultural waste, which can greatly contribute to reducing PHA production costs. Production costs can be minimized by combining the use of agricultural waste as feedstock and the integration of a mixed-culture process into an AD-based technology [1]. For example, fermentations of hydrolyzed whey permeate and the liquid phase of glycerol from biodiesel production were investigated [140]. A poly[3(hydroxybutyrate-co-hydroxyvalerate)] copolyester was produced from both carbon sources without any precursors. A constant 3-hydroxyvalerate amount ($8-10\%$) was obtained, and the total PHA concentrations were 5.5 g/L (whey permeate) and 16.2 g/L (glycerol).

Bioplastics are derived from renewable biomass sources, such as vegetable fats and oils, corn starch, straw, wood crisps, sawdust, and recycled food waste [141]. They are produced through various biological and chemical processes that transform these biomass sources into polymers suitable for making plastics [142]. Bioplastics are used in a variety of products, including packaging materials, bags, utensils, straws, and even some automotive and electronic components. Unlike conventional plastics, many bioplastics are biodegradable or compostable, offering potential benefits in reducing plastic waste and pollution [143]. However, the impact of bioplastics on the environment depends on their specific compositions and end-of-life scenarios.

3.2. Production of Biochar

Biochar, a solid carbon-rich product, is produced in a pyrolysis process by heating the biomass to over 250 °C under limited oxygen conditions. Biochar is produced from forest waste [144], rice husk and bagasse [145,146], corncob [147], olive pits, olive [146], and other wastes.

Biochar has attracted attention due to its versatile applications in various fields. Its uses range from environmental management and agriculture to energy production and the manufacture of materials. Biochar serves as an effective starting material for the production of catalysts due to its large surface area, porosity, and the presence of functional groups [148]. It is particularly valuable in the purification of synthesis gas, where it helps to remove impurities and tar from the synthesis gas and thus improve the efficiency of gasification processes [149]. In addition, biochar-based catalysts are used in the conversion of synthesis gas into liquid hydrocarbons and as solid acid catalysts for biodiesel production, demonstrating their potential in the renewable energy and biofuels industry.

One of the most widely recognized applications of biochar is as a soil amendment [150]. Its addition to soil can significantly enhance soil quality by increasing water retention, nutrient-holding capacity, and microbial activity [151]. Furthermore, biochar aids in mitigating greenhouse gas emissions from soil, contributing to climate change mitigation efforts [152]. Its stable carbon structure also serves as a long-term carbon sink, thereby reducing the net carbon footprint of agricultural practices.

Biochar exhibits excellent adsorption properties, making it an effective sorbent for the reduction of contaminants in soil and water [153]. Its ability to adsorb heavy metals, organic pollutants, and other hazardous compounds from contaminated sites is particularly valuable in environmental remediation projects [154]. The high surface area and specific surface functional groups of biochar enable it to bind with contaminants, preventing their leaching into groundwater and reducing their bioavailability [155].

The porous structure and surface chemistry of biochar also make it suitable for gas adsorption applications, such as CO_2 capture [156] and H_2 storage [157], potentially reducing the impact of fossil fuel emissions on climate change. Its application in H_2 storage is particularly promising for the development of clean energy carriers and supports the transition to a more sustainable energy system.

Biochar is being explored as a low-cost, renewable fuel in direct carbon fuel cells (DCFCs) [158] and as an efficient anode material in MFCs [159]. In DCFC systems, biochar can directly convert the chemical energy in biomass into electricity, offering a greener alternative to traditional fossil fuels [160]. In MFCs, biochar-based anodes can enhance electricity generation from the biochemical energy in organic waste, highlighting its potential in waste-to-energy technologies [161].

The unique structural properties of biochar, such as its large surface area and electrical conductivity, make it a promising material for supercapacitors [162]. Biochar-based supercapacitors can offer a sustainable and cost-effective solution for energy storage, with applications ranging from portable electronics to electric vehicles [163].

Finally, biochar is an excellent precursor for the production of activated carbon, a material widely used in water treatment, air purification, and chemical processing industries [164]. The activation of biochar enhances its adsorptive properties, making it more effective in removing pollutants and impurities from various media.

3.3. Production of Hydrochar

Hydrothermal carbonization (HTC) presents a promising technology for converting wet organic wastes, such as the liquid fraction of digestate, into hydrochar—a carbon-rich solid with coal-like properties [165]. This process not only provides a sustainable approach to waste management, but also creates a valuable product with multiple applications in energy production, agriculture and environmental remediation, representing a significant step forward in circular economy initiatives.

The HTC process emulates natural coal formation but accelerates it significantly, operating under controlled conditions of high temperature (180 °C to 250 °C) and pressure for several hours [166]. This environment breaks down organic molecules into smaller units and facilitates their re-polymerization into complex structures [167]. Subsequently, the mixture is cooled, allowing for the separation of solid hydrochar from the process water and other liquid by-products. The hydrochar undergoes drying to reduce the moisture content, thus enhancing its stability and energy content [168].

The advantages of HTC are manifold. It drastically reduces the volume and mass of organic waste, making disposal or further utilization more manageable [169]. Hydrochar, with its higher calorific value compared to the original waste material, emerges as a viable renewable energy source [170]. Additionally, by converting carbon into a stable solid form, HTC plays a crucial role in carbon sequestration, contributing to the mitigation of greenhouse gas emissions [171]. The process water from HTC, enriched with nutrients, offers potential for treatment and reuse, further supporting water conservation and nutrient recovery efforts. Hydrochar's high calorific value allows it to be used as a solid fuel in industrial

processes or for electricity generation, comparable to coal [172]. Moreover, hydrochar's porous structure makes it an effective medium for water and air purification [173], and it can be incorporated into building materials, plastics, and composites, thus improving their strength and environmental footprint [174].

Despite these benefits, HTC faces challenges, including feedstock variability affecting hydrochar quality, the need for process optimization to improve efficiency and yield, economic hurdles related to high operational costs and scalability, and environmental concerns regarding pollutant release and by-product management. Addressing these issues is crucial for advancing HTC as a sustainable biomass conversion technology [175].

Current research is directed towards optimizing HTC process conditions [176], improving hydrochar quality for specific uses, and integrating HTC into existing waste management frameworks to enhance both environmental and economic outcomes.

3.4. Production of Platform Chemicals

Lignocellulosic biomass is converted into pentoses and hexoses, which, in turn, can be converted into various platform chemicals. Platform chemicals are basic building blocks of the chemical industry and are widely used in the production of food, pharmaceuticals, cosmetics, animal feed, textile products, plasticizers, coating materials, etc. Platform chemicals include lactic acid, succinic acid, maleic acid, levulinic acid, fumaric acid, 3-hydroxypropionic acid, 2,5-furandicarboxylic acid, aspartic acid, glucaric acid, glutamic acid furfural, hydroxymethylfurfural, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol [177,178].

One example of the processing of hemicellulose-rich waste biomass is the catalytic conversion of pentosans into furfural, which has great market potential. Furfural has a carbonyl group and a system of conjugated double bonds in the ring, which enables its effective transformation into chemical products such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran, or alkanes. Furfural itself is not chemically stable (it is easily polymerized), but its other conversion products are chemicals, fuel additives, and alternative fuels desired by industry [26]. The value of furfural in the global market was USD 662 million in 2023 and is estimated to reach up to USD 767 million in 2028 [179]. The C5 sugar platform has been identified as a potential alternative for the generation of furfural and biogas [27].

In addition, the biobutanol industry generates a wide range of value-added by-products, including solvents, coatings, fibers, and plastics, and it serves as a precursor for chemicals such as acrylic acid or butyl acetate [25].

Agricultural waste is a source of other bioactive compounds with high added value, such as polyphenolic compounds as an example. Polyphenolic compounds have been recovered mainly from distillery stillage [16] and olive mill and winery waste [180], and, due to their antioxidant properties, they find applications in the pharmaceutical, cosmetic, and food industries.

3.5. Production of Cellulose Nanomaterials and Nanocomposites

Since about 32–65% of agricultural waste consists of cellulose, this waste is excellent feedstock for cellulose extraction to produce cellulose nanomaterials and nanocomposites with high economic and environmental benefits, particularly in agriculture, medicine, and food packaging [181,182]. This is due to the properties of nanocrystalline cellulose such as optical transparency, high mechanical strength, insolubility in water, and organic solvents and biorenewability, which make nanocellulose-based structures suitable natural materials to produce superabsorbent hydrogels [183], energy storage systems, photovoltaic devices, catalyst components, or mechanical energy harvesters [184].

Various agricultural wastes can serve as sources for the production of cellulose nanomaterials [14]. Several physicochemical, physical, chemical, and biological methods have been investigated to extract cellulose from waste. When selecting these methods, it should

be considered that hemicellulose and lignin inhibit cellulose extraction [22], which is why they should be removed during cellulose extraction.

As wheat straw is the second largest lignocellulosic material in the world [22], it is the main substrate for the production of cellulose nanomaterials and nanocomposites. Other substrates include sugarcane bagasse, rice straw, or algae. For wheat straw and its solid pulp residues, p-toluenesulfonic acid hydrolysis was used to produce lignocellulosic nanofibrils (LCNFs), followed by alkaline peroxide post-treatment to purify LCNFs [185]. Besides LCNFs, wheat straw is a precursor for the production of oxidized cellulose nanofibers, lignocellulose nanofibers, mechanically driven cellulose nanofibers, and cellulose nanocrystals (CNCs). These nanomaterials were blended with carboxymethyl cellulose to produce nanocomposites [186].

CNCs were also prepared from rice-straw-derived cellulose by acid hydrolysis; a high yield of 90.28% was obtained at 30 °C, a time of 5 h, and an acid concentration of 75 wt% [187]. Sulfuric acid hydrolysis of pure cellulose extracted from rice straw, cotton, and grape skin yielded high-quality CNCs in 45, 60, and 30 min, respectively [188]. Sugarcane bagasse is another substrate for producing CNCs, microcrystalline cellulose, or cellulose nanofibers due to its 40–50% cellulose content [189,190]. When producing CNCs by enzymatic hydrolysis from sugarcane bagasse and straw, a high crystallinity index and high thermal stability of the nanomaterials produced were achieved; increasing the duration of enzymatic hydrolysis increased the content of the product but decreased its length and diameter [191]. In addition, the post-processing stream is rich in sugars that can be used for, e.g., ethanol production.

4. Pretreatment of Agricultural Waste

4.1. Recalcitrant Compounds in Biomass

The presence of recalcitrant compounds in the feedstock poses a significant challenge to the AD process [192]. Recalcitrants are complex organic molecules that resist microbial and enzymatic degradation, thereby limiting the conversion efficiency of biomass into biogas [193]. Recalcitrant compounds have been derived from a variety of sources, including lignocellulosic biomass, industrial waste, and agricultural residues [194]. They are characterized by their robust chemical structures, such as aromatic rings and heterocyclic compounds, which render them resistant to the biological processes that drive AD [195]. The persistence of these compounds not only reduces the overall yield of biogas but also can lead to the accumulation of toxic intermediates, further inhibiting microbial activity and prolonging the lag phase of CH_4 production [196].

Furan derivatives are a class of heterocyclic organic compounds consisting of a five-membered aromatic ring with four carbon atoms and one oxygen atom [197]. These compounds, such as furfural and 5-hydroxymethylfurfural (HMF), are often formed during the thermal decomposition of sugars and are particularly prevalent in the pretreatment of lignocellulosic biomass for AD [198]. Furan derivatives are known for their antimicrobial properties, which can inhibit the microbial consortia essential for efficient biogas production [199]. Furfural is produced from pentose sugars found in hemicellulose, and it is a common recalcitrant that is toxic to many microorganisms involved in AD [200]. HMF is derived from hexose sugars, and it is another inhibitor of microbial activity, impacting the overall efficiency of AD [201].

Phenolic compounds are a significant group of recalcitrants characterized by an aromatic ring structure bearing one or more hydroxyl (-OH) groups [202]. These compounds originate from the lignin component of biomass and can significantly hinder microbial activity in AD [203]. Phenolics such as vanillin, syringaldehyde, and 4-hydroxybenzoic acid are known for their antimicrobial and toxic effects, which can reduce the viability of AD microbial communities [204]. Vanillin and syringaldehyde are products of lignin breakdown and are known to be toxic to microorganisms, affecting CH_4 production rates [205]. 4-hydroxybenzoic acid can accumulate during the degradation of lignin and impact the AD process by inhibiting microbial growth [206].

Weak organic acids, such as acetic acid, formic acid, and levulinic acid, are characterized by their carboxylic acid functional group [207]. Though these acids are intermediate products in the AD process and can be utilized by methanogens for CH_4 production, in high concentrations, they can become inhibitory [208]. Their accumulation can lead to acidification of the AD environment, inhibiting methanogenic activity and thus slowing down the biogas production process. Acetic acid is a direct substrate for methanogens; its excessive levels can lead to acidosis in the digester. Formic and levulinic acids can accumulate from the incomplete breakdown of biomass and, in high concentrations, inhibit the methanogenesis stage [209].

The primary adverse effect of recalcitrant compounds is their impact on biogas production. Biogas, primarily consisting of CH_4 and CO_2, is produced when microorganisms break down organic matter under anaerobic conditions. However, recalcitrant materials such as lignin, certain plastics, and complex organics are not easily decomposed, leading to a reduced substrate availability for methane production. This results in lower biogas yields, undermining the energy output and economic viability of biogas plants [210].

The accumulation of recalcitrant compounds can also lead to physical and biochemical instability within the digester [211]. Physically, the build up of undigested materials can cause blockages and impair the mixing within the digester, leading to uneven gas production and possible system shutdowns. Biochemically, these compounds can alter the microbial ecosystem by disproportionately supporting certain bacterial groups over methanogens, which are crucial for CH_4 production. This imbalance can result in operational issues like acid accumulation, foaming, and floating scum, which can interrupt continuous operation [212].

Some recalcitrant compounds have inhibitory effects on the microbial communities responsible for anaerobic digestion [213]. These inhibitors can be natural, such as tannins and phenols from plant materials, or synthetic, from industrial chemicals and residues. Their presence can suppress the metabolic activities of methanogenic Archaea and other beneficial bacteria, further reducing the efficiency of biogas production.

To mitigate these adverse effects, various strategies can be employed. Pretreatment techniques such as thermal, chemical, and enzymatic treatments can be used to break down recalcitrant compounds before they enter the AD system, enhancing their biodegradability (Figure 1). Optimizing the microbial consortium by adding specialized microbes capable of degrading tough compounds can also improve breakdown rates. Regular monitoring and adaptive management of the digester's operational parameters (like pH, temperature, and organic loading rate) can help maintain a balanced microbial ecosystem and efficient system operation.
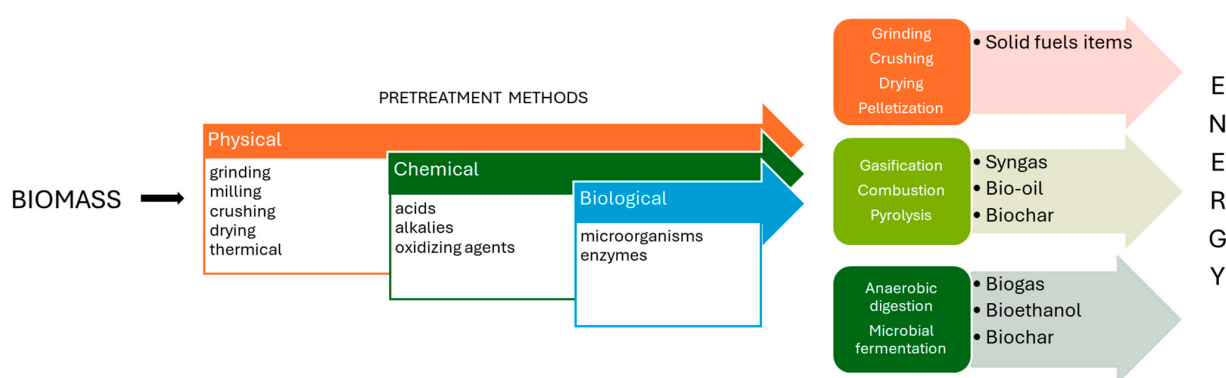

Figure 1. Biomass conversion to energy.

4.2. Reduction in Biogas Yield

Recalcitrant compounds are characterized by their resistance to microbial degradation. This resistance limits the availability of substrates for the microorganisms involved in AD, thereby directly impacting the biogas yield. Essential steps in the biogas production process, such as hydrolysis and acidogenesis, can be inhibited, resulting in a decreased conversion of organic matter into CH_4 and CO_2. For instance, phenolic compounds and furan derivatives

can inhibit key enzyme activities or microbial growth, leading to a reduced rate of substrate breakdown and biogas formation [214].

The presence of recalcitrants can prolong the lag phase, which is the initial period of the AD process before CH_4 production begins [215]. During this phase, the microbial community adapts to the substrate and environmental conditions. Inhibition caused by recalcitrant compounds, such as certain phenolic compounds and furan derivatives, results in a longer time required for the microbial community to establish and commence the efficient conversion of substrates into biogas [216,217]. The prolonged lag phase not only delays the onset of biogas production but can also increase the overall duration of the AD process, affecting the throughput and efficiency of AD facilities.

4.3. Impact of Pretreatment Methods on Recalcitrant Formation

Physical pretreatment methods, such as grinding, milling, and thermal treatments, aim to reduce particle size and increase the surface area of the biomass for microbial access. While these methods can enhance the biodegradability of the substrate, high-temperature treatments (>160 °C) can also lead to the formation of recalcitrants such as furan derivatives (e.g., furfural and HMF) from the degradation of sugars [218]. Although physical pretreatment generally promotes biomass breakdown, excessive temperatures can induce the formation of compounds that are more resistant to microbial action, potentially inhibiting AD. The advantages of mechanical pretreatment are simple and easy operation, no inhibitor produced, reduced crystallinity, enhanced enzyme digestibility, increased porosity, biomass size reduction, and low investment costs. Its disadvantages are high operational costs due to high energy consumption, no lignin degradation, a low sugar yield, and the need to combine with other pretreatments. Thermal pretreatment is a highly reliable method; however, it may generate toxins and inhibitors [219].

Chemical pretreatments involve the use of acids, alkalis, or oxidizing agents to break down the complex structures of biomass, particularly lignin and hemicellulose [220]. While effective in enhancing digestibility, acidic pretreatments can lead to the hydrolysis and solubilization of phenolic compounds, increasing the concentration of these recalcitrants in the substrate [221]. Similarly, alkaline pretreatments can disrupt lignin structures but may also result in the formation of new, more resistant aromatic compounds [222]. The balance between breaking down complex biomass components and avoiding the formation of inhibitory recalcitrants is crucial in chemical pretreatment processes. The advantages of chemical pretreatments include short reaction time, high rate of delignification, decomposition of hemicellulose, reduction in biomass crystallinity and polymerization, low operating temperature, high selectivity, and low costs. Their disadvantages include high toxicity and corrosiveness, formation of inhibitors, possibility of condensation and redistribution of lignin, and environment pollution [219].

Biological pretreatment employs microorganisms or enzymes to degrade lignocellulosic biomass selectively [223]. This method is considered more environmentally friendly and less likely to produce recalcitrant by-products than physical and chemical pretreatments. However, the efficiency of biological pretreatment can be influenced by the presence of naturally occurring recalcitrants within the biomass, which can inhibit the activity of the degrading enzymes or microorganisms [216]. Optimizing the conditions for biological pretreatment is essential to minimize the impact of existing recalcitrants while avoiding the generation of new inhibitors. The advantages of biological pretreatment are mild conditions, low production of hazardous chemicals, and low energy consumption. Its main disadvantages include the long reaction period and low cellulose recovery [219].

Combining different pretreatment methods can leverage the advantages of each approach while mitigating their respective drawbacks. For example, a mild thermal pretreatment followed by enzymatic hydrolysis can reduce the formation of thermal degradation products while efficiently breaking down the biomass [216]. The key to combined pretreatments is to optimize conditions to maximize biomass degradation and the biogas yield without exacerbating the formation of recalcitrants (Table 3).

Table 3. Combined pretreatment methods for intensification of biofuel production.

Pretreatment Method	Mechanism	Substrate	Effects on Digestion	Key Findings	References
Alkali-assisted thermal pretreatment	Utilizes sodium hydroxide (NaOH) to improve the degradation of manure fibers by breaking down recalcitrant compounds like lignin and crystalline cellulose.	Manure fibers	Increased biogas yield and enhanced volatile solids conversion.	CH_4 yield improved by 127% with thermal pretreatment with 3% NaOH added. Optimal reductions in cellulose, hemicellulose, and lignin were 24.8%, 29.1%, and 9.5%, respectively, during pretreatment; 76.5% of cellulose and 84.9% of hemicellulose were converted to CH_4 during AD.	[224]
Thermal hydrolysis pretreatment (THP)	THP enhances the performance of anaerobic digestion by solubilizing and hydrolyzing the organic component of municipal sludge at elevated temperatures and pressures. It involves the Maillard reaction between reducing sugar and amino groups, producing melanoidins, which are recalcitrant dissolved organic nitrogen (rDON) compounds.	Municipal sludge, which typically contains polysaccharides (20–40%) and proteins (30–50%), provides abundant reactants for the Maillard reaction under THP conditions.	Reduction of sludge viscosity, improvement of sludge digestibility and biogas production, enhancement of sludge dewaterability, pathogen sterilization, and odor reduction. Formation of substances with high color and ultraviolet (UV)-quenching ability, inhibition of side-stream nitrogen removal processes, and generation of rDON.	THP at temperatures of 160–190 °C and pressures of 480–1260 kPa leads to the production of melanoidins, a type of rDON.	[225]
Alkali pre-treatment combined with bioaugmentation	Alkali pretreatment disrupts the lignocellulosic structure by breaking down lignin and hemicellulose, which hinders microbial access to cellulose. This increases the porosity, reduces the degree of polymerization, and enhances the surface area for microbial action. Bioaugmentation involves the addition of specific microbial strains or consortia to the digester to target and enhance the degradation of complex organic matter more efficiently.	Lignocellulosic biomass, with grass, is composed mainly of cellulose, hemicellulose, and lignin.	Enhancement of the digestibility of lignocellulosic biomass, leading to increased biogas production. The enhancement in biogas yield is attributed to the more efficient breakdown of the biomass structure, allowing for improved microbial access and activity.	Increases biomethane production by 47% and reduces the retention time from 30 to 20 days, which could significantly lower energy production costs and make the process more economically viable.	[226]

4.4. Mitigation Strategies for Recalcitrants in AD

The management of recalcitrants in AD involves a multifaceted approach, incorporating biological, physical–chemical, and chemical strategies. Each method has its advantages and challenges, and often, a combination of strategies may provide the most effective solution for mitigating the impact of recalcitrants on biogas production.

Biological detoxification is a strategy that leverages specific microorganisms or consortia capable of degrading recalcitrant compounds into less toxic or more biodegradable forms. This approach utilizes the natural metabolic pathways of certain bacteria and fungi, which produce enzymes capable of breaking down complex organic molecules. For instance, white-rot fungi are particularly effective in degrading lignin and its derivatives due to their enzymatic capabilities, including laccases and peroxidases [227]. The advantage of biological detoxification lies in its environmental friendliness and its potential for the complete mineralization of recalcitrant substances. However, effective degradation requires careful selection and optimization of microbial strains and conditions.

Activated carbon adsorption offers a physical–chemical method for recalcitrant removal, utilizing the highly porous nature of activated carbon to adsorb a wide range of organic molecules [228]. This method is effective for reducing the concentrations of various recalcitrant compounds, including phenolics and other toxic substances, thereby mitigating their inhibitory effects on the microbial communities involved in AD [229]. The main advantage of activated carbon adsorption is its broad-spectrum efficacy and ease of integration into existing AD systems. Nonetheless, the need for regular regeneration or replacement of activated carbon can add to the operational costs.

Ion exchange is another technique used to selectively remove recalcitrants from AD feedstock or effluent [230]. By employing resin materials that exchange ions based on their charge properties, this method can effectively target and remove charged molecules such as weak organic acids. Ion exchange is advantageous for its specificity and reversibility, which allows for the regeneration of the resins [231]. However, it may require a multi-stage approach to address the diversity of recalcitrants present in AD processes.

Chemical oxidation, including advanced oxidation processes, involves the use of oxidizing agents to break down recalcitrant compounds into smaller, more biodegradable molecules [232]. Agents such as ozone, hydrogen peroxide, and Fenton's reagent can generate highly reactive hydroxyl radicals capable of degrading a wide range of organic pollutants [233]. This method is notable for its effectiveness across a broad spectrum of recalcitrants and its potential to reduce toxicity significantly. However, the operational costs and the possibility of generating secondary pollutants are considerations that must be managed carefully.

Calcium oxide treatment is a relatively simple and cost-effective method for neutralizing acidic recalcitrants, such as weak organic acids, thereby improving the pH balance in the AD system [234]. By reducing acidification, this approach can enhance microbial activity and CH_4 production. While calcium oxide treatment is advantageous for its low cost and effectiveness in improving the buffer capacity of AD systems, careful dosing is required to avoid excessive alkalinity, which could also inhibit the AD process [235].

5. Conclusions, Challenges, and Perspectives

The global shift to renewable energy sources has highlighted the importance of biofuels as an alternative to fossil fuels. From an ecological point of view, biofuels make a significant contribution to reducing greenhouse gas emissions. Unlike fossil fuels, the CO_2 released during the combustion of biofuels is roughly equivalent to the amount absorbed by the biomass during its growth, resulting in a more balanced carbon cycle. Furthermore, bioproducts such as biochar have the added benefit of sequestering carbon in the soil, actively removing CO_2 from the atmosphere and thus contributing directly to climate change mitigation. In addition to their carbon-neutral potential, the use of biofuels and bioproducts supports sustainable waste management practices. Processes such as AD

convert organic waste into valuable energy sources such as biogas, while reducing the environmental impact associated with landfill disposal.

The main trends in bioenergy production include investigations for maximizing the conversion of agricultural waste on a large scale using cost-effective methods. Searching for cost-effective and easy methods to extract sugars, which can serve as carbon sources for microbial fermentation, is of particular interest. In addition, hydrolysis of lignocellulosic materials by pretreatment for the removal of lignin and hemicellulose is still considered a component of technology that needs to be improved. In particular, in the area of biomass pretreatment, optimizing the composition of the enzyme cocktails for lignocellulose degradation has been the subject of many studies. All these approaches aim at increasing the economic sustainability of the biorefinery.

Economically, biofuels offer a route to greater energy security by diversifying energy sources. This is particularly important for countries with abundant biomass resources, as it allows them to produce energy domestically and insulate themselves from the volatility of global oil markets. In addition, the biofuel and bioproduct industries are catalysts for job creation and economic development in rural areas. They offer new opportunities for farmers, create jobs in processing and manufacturing, and stimulate innovation in related technological areas.

On a societal level, the switch to biofuels can lead to improved public health through better air quality. Since biofuels emit fewer air pollutants compared to fossil fuels, they help reduce the incidence of respiratory and cardiovascular diseases related to air pollution. In addition, the pursuit of renewable energy sources and sustainable materials promotes innovation and technological progress. Research and development efforts in this sector are leading to more efficient biomass conversion technologies, improved feedstock varieties, and the production of novel bioproducts, all of which contribute to a more sustainable and technologically advanced future.

Future research should focus on conducting comprehensive life cycle analyses (LCAs) of recovery routes, to assess their environmental impact and sustainability. There is a growing interest in integrating digestate treatment processes with renewable energy systems to minimize energy requirements and improve overall sustainability. Market development for utilized products is another important area aimed at overcoming barriers to market penetration and acceptance. In addition, exploring policy and regulatory frameworks that support innovation and the adoption of valorization technologies is critical to fostering a favorable environment for digestate valorization.

Advances in biotechnology and molecular biology are opening up promising avenues for the development of specific enzymes that can target recalcitrant compounds in raw materials for AD. This approach is based on the creation of enzymes with increased specificity and efficiency that are able to combat difficult molecules such as lignin derivatives, furan compounds, and phenols. The possibility of using genetically engineering microorganisms to produce these specialized enzymes directly in AD systems could significantly improve the biodegradability of various feedstocks. While the prospect of tailoring enzyme cocktails to specific feedstocks and operating conditions is tantalizing, it is held back by the high production costs and logistical challenges associated with enzyme recovery and reuse, which are critical to economic viability.

Nanotechnology offers innovative solutions for the detoxification of recalcitrant compounds. Nanocatalysts and nanoparticles are used to either degrade complex organic molecules or adsorb substances that inhibit the AD process. This method promises high efficiency and specificity and could revolutionize the handling of recalcitrant substances. However, the application of nanotechnology in AD processes is not without challenges, especially with regard to the environmental impact and the fate of nanomaterials in AD ecosystems, which remain a concern.

The integration of advanced pretreatment technologies into AD systems represents a holistic strategy for dealing with recalcitrant materials. By developing processes that both mitigate the formation of residues during pretreatment and optimize conditions

for microbial digestion, such integrated systems can potentially reduce operating costs while increasing biogas yields. This synergy between thermal, chemical, and biological pretreatment methods could improve the sustainability and efficiency of the AD process. However, the complexity of developing these integrated systems and the need for precise operational management pose a major challenge.

Research into bioelectrochemical systems, as a novel method for dealing with recalcitrant substances in AD, involves the use of electroactive bacteria to directly oxidize recalcitrant compounds. This not only reduces their inhibitory effect on AD but also generates an electric current that could further stimulate the degradation of organic matter. While this approach offers promising prospects for increasing the efficiency of biogas production, it is characterized by technical complexity and a high need for research to optimize system performance and ensure scalability.

Finally, the application of machine learning (ML) and artificial intelligence (AI) to optimize AD processes represents a groundbreaking direction for dealing with recalcitrants. By analyzing complex datasets, ML and AI can uncover patterns and predict the outcomes of different operational strategies, enabling the fine-tuning of pretreatment methods, microbial consortia, and process parameters. This data-driven approach aims to maximize efficiency and minimize the impact of recalcitrant materials, although it requires extensive data collection and the development of accurate predictive models.

Taken together, these new strategies offer a multi-faceted approach to improving the management of residues in AD processes. Each of these strategies has its own perspectives and challenges that need to be addressed to realize their full potential.

In addition, to overcome the challenges with the use of agricultural wastes that hinder their sustainable implementation at the commercial level, fourth-generation biofuels should be further investigated using techniques like nanotechnology, co-culturing, or genetically modified organisms.

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References

1. Gontard, N.; Sonesson, U.; Birkved, M.; Majone, M.; Bolzonella, D.; Celli, A.; Angellier-Coussy, H.; Jang, G.-W.; Verniquet, A.; Broeze, J.; et al. A Research Challenge Vision Regarding Management of Agricultural Waste in a Circular Bio-Based Economy. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48*, 614–654. [CrossRef]
2. Raut, N.A.; Kokare, D.M.; Randive, K.R.; Bhanvase, B.A.; Dhoble, S.J. Introduction: Fundamentals of Waste Removal Technologies. In *360-Degree Waste Management, Volume 1: Fundamentals, Agricultural and Domestic Waste, and Remediation*; Elsevier: Amsterdam, The Netherlands, 2023; pp. 1–16. [CrossRef]
3. Pattanaik, L.; Pattnaik, F.; Saxena, D.K.; Naik, S.N. Biofuels from Agricultural Wastes. In *Second and Third Generation of Feedstocks: The Evolution of Biofuels*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 103–142. [CrossRef]
4. Awasthi, M.K.; Sindhu, R.; Sirohi, R.; Kumar, V.; Ahluwalia, V.; Binod, P.; Juneja, A.; Kumar, D.; Yan, B.; Sarsaiya, S.; et al. Agricultural Waste Biorefinery Development towards Circular Bioeconomy. *Renew. Sustain. Energy Rev.* **2022**, *158*, 112122. [CrossRef]
5. Babu, S.; Singh Rathore, S.; Singh, R.; Kumar, S.; Singh, V.K.; Yadav, S.K.; Yadav, V.; Raj, R.; Yadav, D.; Shekhawat, K.; et al. Exploring Agricultural Waste Biomass for Energy, Food and Feed Production and Pollution Mitigation: A Review. *Bioresour. Technol.* **2022**, *360*, 127566. [CrossRef]
6. Pointner, M.; Kuttner, P.; Obrlik, T.; Jäger, A.; Kahr, H. Composition of Corncobs as a Substrate for Fermentation of Biofuels. *Agron. Res.* **2014**, *12*, 391–396.
7. Panpatte, D.G.; Jhala, Y.K. Agricultural Waste: A Suitable Source for Biofuel Production. In *Prospects of Renewable Bioprocessing in Future Energy Systems*; Springer: Cham, Switzerland, 2019; pp. 337–355.
8. Puligundla, P.; Mok, C. Valorization of Sugar Beet Pulp through Biotechnological Approaches: Recent Developments. *Biotechnol. Lett.* **2021**, *43*, 1253–1263. [CrossRef] [PubMed]
9. Khan, N.; Sudhakar, K.; Mamat, R. Role of Biofuels in Energy Transition, Green Economy and Carbon Neutrality. *Sustainability* **2021**, *13*, 12374. [CrossRef]
10. Kaur, G.; Yadav, N.; Kumar, S. Anaerobic Digestion: A Sustainable Biochemical Approach to Convert Biomass to Bioenergy. In *Biomass Energy for Sustainable Development*; CRC Press: Boca Raton, FL, USA, 2024; pp. 111–126. [CrossRef]

11.   EBA Statistical Report 2023. Available online: https://www.europeanbiogas.eu/eba-statistical-report-2023/ (accessed on 25 March 2024).

12.   Li, C.; Zhao, X.; Wang, A.; Huber, G.W.; Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.* **2015**, *115*, 11559–11624. [CrossRef]

13.   José Horst, D.; Jairo Ramírez Behainne, J.; Paulo de Andrade Junior, P. Lignin as Alternative Fuel: An Estimate of the Thermal Energy Generation Potential from Brazilian Crops. *Environ. Prog. Sustain. Energy* **2017**, *36*, 717–722. [CrossRef]

14.   Gallegos, A.M.A.; Herrera Carrera, S.; Parra, R.; Keshavarz, T.; Iqbal, H.M.N. Bacterial Cellulose: A Sustainable Source to Develop Value-Added Products—A Review. *Bioresources* **2016**, *11*, 5641–5655. [CrossRef]

15.   Harshwardhan, K.; Upadhyay, K. Effective Utilization of Agricultural Waste: Review. *J. Fundam. Renew. Energy Appl.* **2017**, *7*, 5. [CrossRef]

16.   Mikucka, W.; Witońska, I.; Zielińska, M.; Bułkowska, K.; Binczarski, M. Concept for the Valorization of Cereal Processing Waste: Recovery of Phenolic Acids by Using Waste-Derived Tetrahydrofurfuryl Alcohol and Biochar. *Chemosphere* **2023**, *313*, 137457. [CrossRef] [PubMed]

17.   Jimenez-Lopez, C.; Fraga-Corral, M.; Carpena, M.; García-Oliveira, P.; Echave, J.; Pereira, A.G.; Lourenço-Lopes, C.; Prieto, M.A.; Simal-Gandara, J. Agriculture Waste Valorisation as a Source of Antioxidant Phenolic Compounds within a Circular and Sustainable Bioeconomy. *Food Funct.* **2020**, *11*, 4853–4877. [CrossRef] [PubMed]

18.   Riyadi, T.W.B.; Spraggon, M.; Herawan, S.G.; Idris, M.; Paristiawan, P.A.; Putra, N.R.; Faizullizam R, M.; Silambarasan, R.; Veza, I. Biodiesel for HCCI Engine: Prospects and Challenges of Sustainability Biodiesel for Energy Transition. *Results Eng.* **2023**, *17*, 100916. [CrossRef]

19.   Kumar, A.; Kumar, N.; Baredar, P.; Shukla, A. A Review on Biomass Energy Resources, Potential, Conversion and Policy in India. *Renew. Sustain. Energy Rev.* **2015**, *45*, 530–539. [CrossRef]

20.   Cherwoo, L.; Gupta, I.; Flora, G.; Verma, R.; Kapil, M.; Arya, S.K.; Ravindran, B.; Khoo, K.S.; Bhatia, S.K.; Chang, S.W.; et al. Biofuels an Alternative to Traditional Fossil Fuels: A Comprehensive Review. *Sustain. Energy Technol. Assess.* **2023**, *60*, 103503. [CrossRef]

21.   Saravanan, A.; Senthil Kumar, P.; Jeevanantham, S.; Karishma, S.; Vo, D.V.N. Recent Advances and Sustainable Development of Biofuels Production from Lignocellulosic Biomass. *Bioresour. Technol.* **2022**, *344*, 126203. [CrossRef]

22.   Riseh, R.S.; Vazvani, M.G.; Hassanisaadi, M.; Thakur, V.K. Agricultural Wastes: A Practical and Potential Source for the Isolation and Preparation of Cellulose and Application in Agriculture and Different Industries. *Ind. Crops Prod.* **2024**, *208*, 117904. [CrossRef]

23.   Kabeyi, M.J.B.; Olanrewaju, O.A. Biogas Production and Applications in the Sustainable Energy Transition. *J. Energy* **2022**, *2022*, 8750221. [CrossRef]

24.   Deena, S.R.; Vickram, A.S.; Manikandan, S.; Subbaiya, R.; Karmegam, N.; Ravindran, B.; Chang, S.W.; Awasthi, M.K. Enhanced Biogas Production from Food Waste and Activated Sludge Using Advanced Techniques—A Review. *Bioresour. Technol.* **2022**, *355*, 127234. [CrossRef]

25.   Blasi, A.; Verardi, A.; Lopresto, C.G.; Siciliano, S.; Sangiorgio, P. Lignocellulosic Agricultural Waste Valorization to Obtain Valuable Products: An Overview. *Recycling* **2023**, *8*, 61. [CrossRef]

26.   Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; López Granados, M. Furfural: A Renewable and Versatile Platform Molecule for the Synthesis of Chemicals and Fuels. *Energy Environ. Sci.* **2016**, *9*, 1144–1189. [CrossRef]

27.   Aristizábal-Marulanda, V.; Poveda-Giraldo, J.A.; Cardona Alzate, C.A. Comparison of Furfural and Biogas Production Using Pentoses as Platform. *Sci. Total Environ.* **2020**, *728*, 138841. [CrossRef] [PubMed]

28.   Almomani, F.; Bhosale, R.R. Enhancing the Production of Biogas through Anaerobic Co-Digestion of Agricultural Waste and Chemical Pre-Treatments. *Chemosphere* **2020**, *255*, 126805. [CrossRef]

29.   Dumlu, L.; Ciggin, A.S.; Ručman, S.; Perendeci, N.A. Pretreatment, Anaerobic Codigestion, or Both? Which Is More Suitable for the Enhancement of Methane Production from Agricultural Waste? *Molecules* **2021**, *26*, 4175. [CrossRef] [PubMed]

30.   Abouelenien, F.; Namba, Y.; Kosseva, M.R.; Nishio, N.; Nakashimada, Y. Enhancement of Methane Production from Co-Digestion of Chicken Manure with Agricultural Wastes. *Bioresour. Technol.* **2014**, *159*, 80–87. [CrossRef]

31.   Galí, A.; Benabdallah, T.; Astals, S.; Mata-Alvarez, J. Modified Version of ADM1 Model for Agro-Waste Application. *Bioresour. Technol.* **2009**, *100*, 2783–2790. [CrossRef] [PubMed]

32.   Chandra, R.; Takeuchi, H.; Hasegawa, T. Methane Production from Lignocellulosic Agricultural Crop Wastes: A Review in Context to Second Generation of Biofuel Production. *Renew. Sustain. Energy Rev.* **2012**, *16*, 1462–1476. [CrossRef]

33.   Garcia, N.H.; Mattioli, A.; Gil, A.; Frison, N.; Battista, F.; Bolzonella, D. Evaluation of the Methane Potential of Different Agricultural and Food Processing Substrates for Improved Biogas Production in Rural Areas. *Renew. Sustain. Energy Rev.* **2019**, *112*, 1–10. [CrossRef]

34.   Kalra, M.S.; Panwar, J.S. Anaerobic Digestion of Rice Crop Residues. *Agric. Wastes* **1986**, *17*, 263–269. [CrossRef]

35.   Beniche, I.; El Bari, H.; Siles, J.A.; Chica, A.F.; Martín, M.Á. Methane Production by Anaerobic Co-Digestion of Mixed Agricultural Waste: Cabbage and Cauliflower. *Environ. Technol.* **2021**, *42*, 4550–4558. [CrossRef]

36.   Gunaseelan, V.N. Biochemical Methane Potential of Fruits and Vegetable Solid Waste Feedstocks. *Biomass Bioenergy* **2004**, *26*, 389–399. [CrossRef]

37. Da Ros, C.; Cavinato, C.; Bolzonella, D.; Pavan, P. Renewable Energy from Thermophilic Anaerobic Digestion of Winery Residue: Preliminary Evidence from Batch and Continuous Lab-Scale Trials. *Biomass Bioenergy* **2016**, *91*, 150–159. [CrossRef]
38. Paepatung, N.; Nopharatana, A.; Songkasiri, W. Bio-Methane Potential of Biological Solid Materials and Agricultural Wastes. *Asian J. Energy Environ.* **2009**, *10*, 19–27.
39. Hu, B.; Li, Y.; Zhu, S.; Zhang, H.; Jing, Y.; Jiang, D.; He, C.; Zhang, Z. Evaluation of Biohydrogen Yield Potential and Electron Balance in the Photo-Fermentation Process with Different Initial PH from Starch Agricultural Leftover. *Bioresour. Technol.* **2020**, *305*, 122900. [CrossRef] [PubMed]
40. Yue, T.; Jiang, D.; Zhang, Z.; Zhang, Y.; Li, Y.; Zhang, T.; Zhang, Q. Recycling of Shrub Landscaping Waste: Exploration of Bio-Hydrogen Production Potential and Optimization of Photo-Fermentation Bio-Hydrogen Production Process. *Bioresour. Technol.* **2021**, *331*, 125048. [CrossRef] [PubMed]
41. Zhu, S.; Zhang, Y.; Zhang, Z.; Li, Y.; Ai, F.; Zhang, Q. Effect of Fe0 Particle Size on Buffering Characteristics and Biohydrogen Production in High-Load Photo Fermentation System of Corn Stover. *Bioresour. Technol.* **2022**, *364*, 128086. [CrossRef] [PubMed]
42. Zhang, Z.; Zhang, H.; Li, Y.; Lu, C.; Zhu, S.; He, C.; Ai, F.; Zhang, Q. Investigation of the Interaction between Lighting and Mixing Applied during the Photo-Fermentation Biohydrogen Production Process from Agricultural Waste. *Bioresour. Technol.* **2020**, *312*, 123570. [CrossRef] [PubMed]
43. Sołowski, G.; Konkol, I.; Cenian, A. Methane and Hydrogen Production from Cotton Waste by Dark Fermentation under Anaerobic and Micro-Aerobic Conditions. *Biomass Bioenergy* **2020**, *138*, 105576. [CrossRef]
44. Li, Y.; Zhang, Q.; Deng, L.; Liu, Z.; Jiang, H.; Wang, F. Biohydrogen Production from Fermentation of Cotton Stalk Hydrolysate by Klebsiella Sp. WL1316 Newly Isolated from Wild Carp (Cyprinus Carpio L.) of the Tarim River Basin. *Appl. Microbiol. Biotechnol.* **2018**, *102*, 4231–4242. [CrossRef]
45. Su, H.; Cheng, J.; Zhou, J.; Song, W.; Cen, K. Improving Hydrogen Production from Cassava Starch by Combination of Dark and Photo Fermentation. *Int. J. Hydrog. Energy* **2009**, *34*, 1780–1786. [CrossRef]
46. Smuga-Kogut, M.; Wnuk, A.D.; Zgórska, K.; Kubiak, M.S.; Wojdalski, J.; Kupczyk, A.; Szlachta, J.; Luberański, A. Production of Ethanol from Wheat Straw. *Pol. J. Chem. Technol.* **2015**, *17*, 89–94. [CrossRef]
47. Biswas, B.; Pandey, N.; Bisht, Y.; Singh, R.; Kumar, J.; Bhaskar, T. Pyrolysis of Agricultural Biomass Residues: Comparative Study of Corn Cob, Wheat Straw, Rice Straw and Rice Husk. *Bioresour. Technol.* **2017**, *237*, 57–63. [CrossRef] [PubMed]
48. Kamarudin, S.K.; Shamsul, N.S.; Ghani, J.A.; Chia, S.K.; Liew, H.S.; Samsudin, A.S. Production of Methanol from Biomass Waste via Pyrolysis. *Bioresour. Technol.* **2013**, *129*, 463–468. [CrossRef] [PubMed]
49. Harisankar, S.; Vishnu Mohan, R.; Choudhary, V.; Vinu, R. Effect of Water Quality on the Yield and Quality of the Products from Hydrothermal Liquefaction and Carbonization of Rice Straw. *Bioresour. Technol.* **2022**, *351*, 127031. [CrossRef] [PubMed]
50. Mesa, L.; Martínez, Y.; Celia de Armas, A.; González, E. Ethanol Production from Sugarcane Straw Using Different Configurations of Fermentation and Techno-Economical Evaluation of the Best Schemes. *Renew. Energy* **2020**, *156*, 377–388. [CrossRef]
51. Barbosa, F.C.; Martins, M.; Brenelli, L.B.; Ferrari, F.A.; Forte, M.B.S.; Rabelo, S.C.; Franco, T.T.; Goldbeck, R. Screening of Potential Endoglucanases, Hydrolysis Conditions and Different Sugarcane Straws Pretreatments for Cello-Oligosaccharides Production. *Bioresour. Technol.* **2020**, *316*, 123918. [CrossRef] [PubMed]
52. Hossain, T.; Miah, A.B.; Mahmud, S.A.; Mahin, A.-A. Enhanced Bioethanol Production from Potato Peel Waste Via Consolidated Bioprocessing with Statistically Optimized Medium. *Appl. Biochem. Biotechnol.* **2018**, *186*, 425–442. [CrossRef]
53. Antonopoulou, G.; Vayenas, D.; Lyberatos, G. Ethanol and Hydrogen Production from Sunflower Straw: The Effect of Pretreatment on the Whole Slurry Fermentation. *Biochem. Eng. J.* **2016**, *116*, 65–74. [CrossRef]
54. Gong, L.; Zha, J.; Pan, L.; Ma, C.; He, Y.C. Highly Efficient Conversion of Sunflower Stalk-Hydrolysate to Furfural by Sunflower Stalk Residue-Derived Carbonaceous Solid Acid in Deep Eutectic Solvent/Organic Solvent System. *Bioresour. Technol.* **2022**, *351*, 126945. [CrossRef]
55. Guo, J.; Cui, X.; Sun, H.; Zhao, Q.; Wen, X.; Pang, C.; Dong, R. Effect of Glucose and Cellulase Addition on Wet-Storage of Excessively Wilted Maize Stover and Biogas Production. *Bioresour. Technol.* **2018**, *259*, 198–206. [CrossRef]
56. Buaban, B.; Inoue, H.; Yano, S.; Tanapongpipat, S.; Ruanglek, V.; Champreda, V.; Pichyangkura, R.; Rengpipat, S.; Eurwilaichitr, L. Bioethanol Production from Ball Milled Bagasse Using an On-Site Produced Fungal Enzyme Cocktail and Xylose-Fermenting Pichia Stipitis. *J. Biosci. Bioeng.* **2010**, *110*, 18–25. [CrossRef] [PubMed]
57. Shafiei Alavijeh, R.; Karimi, K.; van den Berg, C. An Integrated and Optimized Process for Cleaner Production of Ethanol and Biodiesel from Corn Stover by Mucor Indicus. *J. Clean. Prod.* **2020**, *249*, 119321. [CrossRef]
58. Zhang, J.; Wang, Y.; Gou, Q.; Zhou, W.; Liu, Y.; Xu, J.; Liu, Y.; Zhou, W.; Gong, Z. Consolidated Bioprocessing of Cassava Starch into Microbial Lipid for Biodiesel Production by the Amylolytic Yeast Lipomyces Starkeyi. *Ind. Crops Prod.* **2022**, *177*, 114534. [CrossRef]
59. Ibrahim, H.; Silitonga, A.S.; Rahmawaty, R.; Dharma, S.; Sebayang, A.H.; Khairil, K.; Sumartono, S.; Sutrisno, J.; Razak, A. An Ultrasound Assisted Transesterification to Optimize Biodiesel Production from Rice Bran Oil. *Int. J. Technol.* **2020**, *11*, 225. [CrossRef]
60. Wu, L.; Wei, W.; Song, L.; Woźniak-Karczewska, M.; Chrzanowski, Ł.; Ni, B.J. Upgrading Biogas Produced in Anaerobic Digestion: Biological Removal and Bioconversion of CO_2 in Biogas. *Renew. Sustain. Energy Rev.* **2021**, *150*, 111448. [CrossRef]
61. Mulu, E.; M'Arimi, M.M.; Ramkat, R.C. A Review of Recent Developments in Application of Low Cost Natural Materials in Purification and Upgrade of Biogas. *Renew. Sustain. Energy Rev.* **2021**, *145*, 111081. [CrossRef]

62. Muntaha, N.; Rain, M.I.; Goni, L.K.M.O.; Shaikh, M.A.A.; Jamal, M.S.; Hossain, M. A Review on Carbon Dioxide Minimization in Biogas Upgradation Technology by Chemical Absorption Processes. *ACS Omega* **2022**, *7*, 33680–33698. [CrossRef] [PubMed]

63. Bahrun, M.H.V.; Bono, A.; Othman, N.; Zaini, M.A.A. Carbon Dioxide Removal from Biogas through Pressure Swing Adsorption— A Review. *Chem. Eng. Res. Des.* **2022**, *183*, 285–306. [CrossRef]

64. Gkotsis, P.; Kougias, P.; Mitrakas, M.; Zouboulis, A. Biogas Upgrading Technologies—Recent Advances in Membrane-Based Processes. *Int. J. Hydrog. Energy* **2023**, *48*, 3965–3993. [CrossRef]

65. Ahmed, S.F.; Mofijur, M.; Tarannum, K.; Chowdhury, A.T.; Rafa, N.; Nuzhat, S.; Kumar, P.S.; Vo, D.V.N.; Lichtfouse, E.; Mahlia, T.M.I. Biogas Upgrading, Economy and Utilization: A Review. *Environ. Chem. Lett.* **2021**, *19*, 4137–4164. [CrossRef]

66. Assunção, R.C.L.; Mendes, A.S.P.; Matos, S.; Borschiver, S. Technology Roadmap of Renewable Natural Gas: Identifying Trends for Research and Development to Improve Biogas Upgrading Technology Management. *Appl. Energy* **2021**, *292*, 116849. [CrossRef]

67. Andlar, M.; Belskaya, H.; Morzak, G.; Šantek, M.I.; Rezić, T.; Tominac, V.P.; Šantek, B. Biogas Production Systems and Upgrading Technologies: A Review. *Food Technol. Biotechnol.* **2021**, *59*, 387–412. [CrossRef] [PubMed]

68. Wassie, Y.T.; Adaramola, M.S. Analysing Household Biogas Utilization and Impact in Rural Ethiopia: Lessons and Policy Implications for Sub-Saharan Africa. *Sci. Afr.* **2020**, *9*, e00474. [CrossRef]

69. Abanades, S.; Abbaspour, H.; Ahmadi, A.; Das, B.; Ehyaei, M.A.; Esmaeilion, F.; El Haj Assad, M.; Hajilounezhad, T.; Hmida, A.; Rosen, M.A.; et al. A Conceptual Review of Sustainable Electrical Power Generation from Biogas. *Energy Sci. Eng.* **2022**, *10*, 630–655. [CrossRef]

70. Zheng, Y.; Zhang, Q.; Zhang, Z.; Jing, Y.; Hu, J.; He, C.; Lu, C. A Review on Biological Recycling in Agricultural Waste-Based Biohydrogen Production: Recent Developments. *Bioresour. Technol.* **2022**, *347*, 126595. [CrossRef] [PubMed]

71. Bundhoo, Z.M.A. Potential of Bio-Hydrogen Production from Dark Fermentation of Crop Residues: A Review. *Int. J. Hydrog. Energy* **2019**, *44*, 17346–17362. [CrossRef]

72. Niño-Navarro, C.; Chairez, I.; Christen, P.; Canul-Chan, M.; García-Peña, E.I. Enhanced Hydrogen Production by a Sequential Dark and Photo Fermentation Process: Effects of Initial Feedstock Composition, Dilution and Microbial Population. *Renew. Energy* **2020**, *147*, 924–936. [CrossRef]

73. Prajapati, K.B.; Singh, R. Bio-Electrochemically Hydrogen and Methane Production from Co-Digestion of Wastes. *Energy* **2020**, *198*, 117259. [CrossRef]

74. Kim, M.; Yang, Y.; Morikawa-Sakura, M.S.; Wang, Q.; Lee, M.V.; Lee, D.-Y.; Feng, C.; Zhou, Y.; Zhang, Z. Hydrogen Production by Anaerobic Co-Digestion of Rice Straw and Sewage Sludge. *Int. J. Hydrog. Energy* **2012**, *37*, 3142–3149. [CrossRef]

75. Zhang, X.; Huo, L.; Yao, Z.; Xie, T.; Sun, Y.; Liu, Z.; Zhao, Y.; Zhao, L. A Comparative Review on the Progress of Thermochemical Hydrogen Production Technologies from Agricultural Waste. *Fuel* **2024**, *366*, 131284. [CrossRef]

76. Rahimi, Z.; Anand, A.; Gautam, S. An Overview on Thermochemical Conversion and Potential Evaluation of Biofuels Derived from Agricultural Wastes. *Energy Nexus* **2022**, *7*, 100125. [CrossRef]

77. Leng, L.; Yang, L.; Chen, J.; Leng, S.; Li, H.; Li, H.; Yuan, X.; Zhou, W.; Huang, H. A Review on Pyrolysis of Protein-Rich Biomass: Nitrogen Transformation. *Bioresour. Technol.* **2020**, *315*, 123801. [CrossRef] [PubMed]

78. Sarkar, N.; Ghosh, S.K.; Bannerjee, S.; Aikat, K. Bioethanol Production from Agricultural Wastes: An Overview. *Renew. Energy* **2012**, *37*, 19–27. [CrossRef]

79. Granjo, J.F.O.; Nunes, D.S.; Duarte, B.P.M.; Oliveira, N.M.C. A Comparison of Process Alternatives for Energy-Efficient Bioethanol Downstream Processing. *Sep. Purif. Technol.* **2020**, *238*, 116414. [CrossRef]

80. Braide, W.; Kanu, I.; Oranusi, U.; Adeleye, S. Production of Bioethanol from Agricultural Waste. *J. Fundam. Appl. Sci.* **2016**, *8*, 372. [CrossRef]

81. Walker, G.M.; Basso, T.O. Mitigating Stress in Industrial Yeasts. *Fungal Biol.* **2020**, *124*, 387–397. [CrossRef]

82. Elfasakhany, A. Gasoline Engine Fueled with Bioethanol-Bio-Acetone-Gasoline Blends: Performance and Emissions Exploration. *Fuel* **2020**, *274*, 117825. [CrossRef]

83. Aliyu, G.; Mshelia, R.B. Review of the Use of Bioethanol as Alternative Fuel for Internal Combustion Engines. *Acta Tech. Corviniensis-Bull. Eng.* **2021**, *14*, 139–144.

84. Sanchez, N.; Ruiz, R.; Hacker, V.; Cobo, M. Impact of Bioethanol Impurities on Steam Reforming for Hydrogen Production: A Review. *Int. J. Hydrog. Energy* **2020**, *45*, 11923–11942. [CrossRef]

85. Bonenkamp, T.B.; Middelburg, L.M.; Hosli, M.O.; Wolffenbuttel, R.F. From Bioethanol Containing Fuels towards a Fuel Economy That Includes Methanol Derived from Renewable Sources and the Impact on European Union Decision-Making on Transition Pathways. *Renew. Sustain. Energy Rev.* **2020**, *120*, 109667. [CrossRef]

86. Erixno, O.; Rahim, N.A.; Ramadhani, F.; Adzman, N.N. Energy Management of Renewable Energy-Based Combined Heat and Power Systems: A Review. *Sustain. Energy Technol. Assess.* **2022**, *51*, 101944. [CrossRef]

87. Passaretti, A.; Cuvillier, L.; Sciutto, G.; Guilminot, E.; Joseph, E. Biologically Derived Gels for the Cleaning of Historical and Artistic Metal Heritage. *Appl. Sci.* **2021**, *11*, 3405. [CrossRef]

88. Ceylan, S.; Potuk, K.; Bayraktar, O. *High-Value–Added Products from Microalgae Production Integrated with Bioethanol Process. Bioenergy Engineering: Fundamentals, Methods, Modelling, and Applications*; Woodhead Publishing: Sawston, UK, 2023; pp. 315–332. [CrossRef]

89. Jamil, F.; Aslam, M.; Al-Muhtaseb, A.H.; Bokhari, A.; Rafiq, S.; Khan, Z.; Inayat, A.; Ahmed, A.; Hossain, S.; Khurram, M.S.; et al. Greener and Sustainable Production of Bioethylene from Bioethanol: Current Status, Opportunities and Perspectives. *Rev. Chem. Eng.* **2022**, *38*, 185–207. [CrossRef]

90. Raj, T.; Chandrasekhar, K.; Naresh Kumar, A.; Kim, S.H. Lignocellulosic Biomass as Renewable Feedstock for Biodegradable and Recyclable Plastics Production: A Sustainable Approach. *Renew. Sustain. Energy Rev.* **2022**, *158*, 112130. [CrossRef]

91. Awogbemi, O.; Von Kallon, D.V.; Aigbodion, V.S. Trends in the Development and Utilization of Agricultural Wastes as Heterogeneous Catalyst for Biodiesel Production. *J. Energy Inst.* **2021**, *98*, 244–258. [CrossRef]

92. Awasthi, P.; Shrivastava, S.; Kharkwal, A.C.; Varma, A. Biofuel from Agricultural Waste: A Review. *Int. J. Curr. Microbiol. App. Sci.* **2015**, *4*, 470–477.

93. Koreti, D.; Kosre, A.; Jadhav, S.K.; Chandrawanshi, N.K. A Comprehensive Review on Oleaginous Bacteria: An Alternative Source for Biodiesel Production. *Bioresour. Bioprocess.* **2022**, *9*, 47. [CrossRef]

94. Kasirajan, L.; Maupin-Furlow, J.A. Halophilic Archaea and Their Potential to Generate Renewable Fuels and Chemicals. *Biotechnol. Bioeng.* **2021**, *118*, 1066–1090. [CrossRef]

95. Safieddin Ardebili, S.M.; Khademalrasoul, A. An Analysis of Liquid-Biofuel Production Potential from Agricultural Residues and Animal Fat (Case Study: Khuzestan Province). *J. Clean. Prod.* **2018**, *204*, 819–831. [CrossRef]

96. Monteiro, M.R.; Kugelmeier, C.L.; Pinheiro, R.S.; Batalha, M.O.; da Silva César, A. Glycerol from Biodiesel Production: Technological Paths for Sustainability. *Renew. Sustain. Energy Rev.* **2018**, *88*, 109–122. [CrossRef]

97. Dias, M.E.S.; Lopes, J.C.; Carneiro, R.B.; Damianovic, M.H.R.Z.; Foresti, E. Using Compounds Derived from the Glycerol Fermentation as a Carbon Source for Denitrification and Biological Phosphorus Removal. *Water Air Soil. Pollut.* **2021**, *232*, 339. [CrossRef]

98. Balwan, W.K.; Kour, S. A Systematic Review of Biofuels: The Cleaner Energy for Cleaner Environment. *Indian. J. Sci. Res.* **2021**, *12*, 135–142. [CrossRef]

99. Ogunkunle, O.; Ahmed, N.A. Overview of Biodiesel Combustion in Mitigating the Adverse Impacts of Engine Emissions on the Sustainable Human–Environment Scenario. *Sustainability* **2021**, *13*, 5465. [CrossRef]

100. Aydın, S. Comprehensive Analysis of Combustion, Performance and Emissions of Power Generator Diesel Engine Fueled with Different Source of Biodiesel Blends. *Energy* **2020**, *205*, 118074. [CrossRef]

101. Khan, F.A.; Pal, N.; Saeed, S.H. *Stand-Alone Hybrid System of Solar Photovoltaics/Wind Energy Resources: An Eco-Friendly Sustainable Approach. Renewable Energy Systems*; Academic Press: Cambridge, MA, USA, 2021; pp. 687–705. [CrossRef]

102. Dey, P.; Ray, S.; Newar, A. Defining a Waste Vegetable Oil-Biodiesel Based Diesel Substitute Blend Fuel by Response Surface Optimization of Density and Calorific Value. *Fuel* **2021**, *283*, 118978. [CrossRef]

103. Ningaraju, C.; Yatish, K.V.; Mithun Prakash, R.; Sakar, M.; Balakrishna, R. Simultaneous Refining of Biodiesel-Derived Crude Glycerol and Synthesis of Value-Added Powdered Catalysts for Biodiesel Production: A Green Chemistry Approach for Sustainable Biodiesel Industries. *J. Clean. Prod.* **2022**, *363*, 132448. [CrossRef]

104. Moradi, F.; Amiri, H.; Soleimanian-Zad, S.; Ehsani, M.R.; Karimi, K. Improvement of Acetone, Butanol and Ethanol Production from Rice Straw by Acid and Alkaline Pretreatments. *Fuel* **2013**, *112*, 8–13. [CrossRef]

105. Cheng, C.L.; Che, P.Y.; Chen, B.Y.; Lee, W.J.; Lin, C.Y.; Chang, J.S. Biobutanol Production from Agricultural Waste by an Acclimated Mixed Bacterial Microflora. *Appl. Energy* **2012**, *100*, 3–9. [CrossRef]

106. Ibrahim, M.F.; Ramli, N.; Kamal Bahrin, E.; Abd-Aziz, S. Cellulosic Biobutanol by Clostridia: Challenges and Improvements. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1241–1254. [CrossRef]

107. Awogbemi, O.; Kallon, D.V. Von Valorization of Agricultural Wastes for Biofuel Applications. *Heliyon* **2022**, *8*, e11117. [CrossRef]

108. Santos, J.; Ouadi, M.; Jahangiri, H.; Hornung, A. Integrated Intermediate Catalytic Pyrolysis of Wheat Husk. *Food Bioprod. Process.* **2019**, *114*, 23–30. [CrossRef]

109. Stigsson, C.; Furusjö, E.; Börjesson, P. A Model of an Integrated Hydrothermal Liquefaction, Gasification and Fischer-Tropsch Synthesis Process for Converting Lignocellulosic Forest Residues into Hydrocarbons. *Bioresour. Technol.* **2022**, *353*, 126070. [CrossRef] [PubMed]

110. Hawash, S.I.; Farah, J.Y.; El-Diwani, G. Pyrolysis of Agriculture Wastes for Bio-Oil and Char Production. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 369–372. [CrossRef]

111. Biswas, B.; Singh, R.; Kumar, J.; Singh, R.; Gupta, P.; Krishna, B.B.; Bhaskar, T. Pyrolysis Behavior of Rice Straw under Carbon Dioxide for Production of Bio-Oil. *Renew. Energy* **2018**, *129*, 686–694. [CrossRef]

112. Wang, Y.; Zeng, Z.; Tian, X.; Dai, L.; Jiang, L.; Zhang, S.; Wu, Q.; Wen, P.; Fu, G.; Liu, Y.; et al. Production of Bio-Oil from Agricultural Waste by Using a Continuous Fast Microwave Pyrolysis System. *Bioresour. Technol.* **2018**, *269*, 162–168. [CrossRef] [PubMed]

113. Liu, S.; Xie, Q.; Zhang, B.; Cheng, Y.; Liu, Y.; Chen, P.; Ruan, R. Fast Microwave-Assisted Catalytic Co-Pyrolysis of Corn Stover and Scum for Bio-Oil Production with CaO and HZSM-5 as the Catalyst. *Bioresour. Technol.* **2016**, *204*, 164–170. [CrossRef]

114. Ravikumar, C.; Senthil Kumar, P.; Subhashni, S.K.; Tejaswini, P.V.; Varshini, V. Microwave Assisted Fast Pyrolysis of Corn Cob, Corn Stover, Saw Dust and Rice Straw: Experimental Investigation on Bio-Oil Yield and High Heating Values. *Sustain. Mater. Technol.* **2017**, *11*, 19–27. [CrossRef]

115. Machado, H.; Cristino, A.F.; Orišková, S.; Galhano dos Santos, R. Bio-Oil: The Next-Generation Source of Chemicals. *Reactions* **2022**, *3*, 118–137. [CrossRef]

116. Sánchez-Borrego, F.J.; Álvarez-Mateos, P.; García-Martín, J.F. Biodiesel and Other Value-Added Products from Bio-Oil Obtained from Agrifood Waste. *Processes* **2021**, *9*, 797. [CrossRef]

117. Premier, G.C.; Kim, J.R.; Massanet-Nicolau, J.; Kyazze, G.; Esteves, S.R.R.; Penumathsa, B.K.V.; Rodríguez, J.; Maddy, J.; Dinsdale, R.M.; Guwy, A.J. Integration of Biohydrogen, Biomethane and Bioelectrochemical Systems. *Renew. Energy* **2013**, *49*, 188–192. [CrossRef]

118. Monlau, F.; Barakat, A.; Trably, E.; Dumas, C.; Steyer, J.-P.; Carrère, H. Lignocellulosic Materials Into Biohydrogen and Biomethane: Impact of Structural Features and Pretreatment. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 260–322. [CrossRef]

119. Rena; Mohammed Bin Zacharia, K.; Yadav, S.; Machhirake, N.P.; Kim, S.H.; Lee, B.D.; Jeong, H.; Singh, L.; Kumar, S.; Kumar, R. Bio-Hydrogen and Bio-Methane Potential Analysis for Production of Bio-Hythane Using Various Agricultural Residues. *Bioresour. Technol.* **2020**, *309*, 123297. [CrossRef] [PubMed]

120. Pandit, S.; Savla, N.; Sonawane, J.M.; Sani, A.M.; Gupta, P.K.; Mathuriya, A.S.; Rai, A.K.; Jadhav, D.A.; Jung, S.P.; Prasad, R. Agricultural Waste and Wastewater as Feedstock for Bioelectricity Generation Using Microbial Fuel Cells: Recent Advances. *Fermentation* **2021**, *7*, 169. [CrossRef]

121. Zuo, Y.; Maness, P.-C.; Logan, B.E. Electricity Production from Steam-Exploded Corn Stover Biomass. *Energy Fuels* **2006**, *20*, 1716–1721. [CrossRef]

122. Wang, Y.-Z.; Shen, Y.; Gao, L.; Liao, Z.-H.; Sun, J.-Z.; Yong, Y.-C. Improving the Extracellular Electron Transfer of Shewanella Oneidensis MR-1 for Enhanced Bioelectricity Production from Biomass Hydrolysate. *RSC Adv.* **2017**, *7*, 30488–30494. [CrossRef]

123. Gurung, A.; Oh, S.-E. Rice Straw as a Potential Biomass for Generation of Bioelectrical Energy Using Microbial Fuel Cells (MFCs). *Energy Sources Part. A Recovery Util. Environ. Eff.* **2015**, *37*, 2625–2631. [CrossRef]

124. Gregoire, K.P.; Becker, J.G. Design and Characterization of a Microbial Fuel Cell for the Conversion of a Lignocellulosic Crop Residue to Electricity. *Bioresour. Technol.* **2012**, *119*, 208–215. [CrossRef] [PubMed]

125. Statistical Report 2022 Development and Implementation of Biogas on the European Market—European Biogas Association (EBA). Available online: https://biometan.org.pl/raport-statystyczny-2022 (accessed on 17 April 2024).

126. Kang, K.E.; Jeong, J.S.; Kim, Y.; Min, J.; Moon, S.K. Development and Economic Analysis of Bioethanol Production Facilities Using Lignocellulosic Biomass. *J. Biosci. Bioeng.* **2019**, *128*, 475–479. [CrossRef]

127. Madian, H.R.; Sidkey, N.M.; Abo Elsoud, M.M.; Hamouda, H.I.; Elazzazy, A.M. Bioethanol Production from Water Hyacinth Hydrolysate by Candida Tropicalis Y-26. *Arab. J. Sci. Eng.* **2019**, *44*, 33–41. [CrossRef]

128. Sondhi, S.; Kaur, P.S.; Kaur, M. Techno-Economic Analysis of Bioethanol Production from Microwave Pretreated Kitchen Waste. *SN Appl. Sci.* **2020**, *2*, 1558. [CrossRef]

129. Barzegaravval, H.; Hosseini, S.E.; Wahid, M.A.; Saat, A. Effects of Fuel Composition on the Economic Performance of Biogas-Based Power Generation Systems. *Appl. Therm. Eng.* **2018**, *128*, 1543–1554. [CrossRef]

130. Abduh, M.Y.; Manurung, R.; Heeres, H.J.; Puad, N.I.M. A Review on Community Scale Stationary and Mobile Production of Biodiesel. *Curr. Res. Biosci. Biotechnol.* **2021**, *2*, 126–138. [CrossRef]

131. Szulczyk, K.R.; Cheema, M.A. The Economic Feasibility and Environmental Ramifications of Biobutanol Production in Malaysia. *J. Clean. Prod.* **2021**, *286*, 124953. [CrossRef]

132. Mukherjee, M.; Goswami, G.; Mondal, P.K.; Das, D. Biobutanol as a Potential Alternative to Petroleum Fuel: Sustainable Bioprocess and Cost Analysis. *Fuel* **2020**, *278*, 118403. [CrossRef]

133. D'Adamo, I.; Ribichini, M.; Tsagarakis, K.P. Biomethane as an Energy Resource for Achieving Sustainable Production: Economic Assessments and Policy Implications. *Sustain. Prod. Consum.* **2023**, *35*, 13–27. [CrossRef]

134. Ahmed, S.F.; Rafa, N.; Mofijur, M.; Badruddin, I.A.; Inayat, A.; Ali, M.S.; Farrok, O.; Yunus Khan, T.M. Biohydrogen Production From Biomass Sources: Metabolic Pathways and Economic Analysis. *Front. Energy Res.* **2021**, *9*, 753878. [CrossRef]

135. Van Nguyen, T.; Clausen, L.R. Techno-Economic Analysis of Polygeneration Systems Based on Catalytic Hydropyrolysis for the Production of Bio-Oil and Fuels. *Energy Convers. Manag.* **2019**, *184*, 539–558. [CrossRef]

136. Righetti, E.; Nortilli, S.; Fatone, F.; Frison, N.; Bolzonella, D. A Multiproduct Biorefinery Approach for the Production of Hydrogen, Methane and Volatile Fatty Acids from Agricultural Waste. *Waste Biomass Valorization* **2020**, *11*, 5239–5246. [CrossRef]

137. Greses, S.; Tomás-Pejó, E.; Gónzalez-Fernández, C. Agroindustrial Waste as a Resource for Volatile Fatty Acids Production via Anaerobic Fermentation. *Bioresour. Technol.* **2020**, *297*, 122486. [CrossRef]

138. Bioplastics Market Development Update 2023. Available online: https://www.european-bioplastics.org/bioplastics-market-development-update-2023-2/ (accessed on 25 March 2024).

139. Wang, J.; Liu, S.; Huang, J.; Qu, Z. A Review on Polyhydroxyalkanoate Production from Agricultural Waste Biomass: Development, Advances, Circular Approach, and Challenges. *Bioresour. Technol.* **2021**, *342*, 126008. [CrossRef]

140. Koller, M.; Bona, R.; Braunegg, G.; Hermann, C.; Horvat, P.; Kroutil, M.; Martinz, J.; Neto, J.; Pereira, L.; Varila, P. Production of Polyhydroxyalkanoates from Agricultural Waste and Surplus Materials. *Biomacromolecules* **2005**, *6*, 561–565. [CrossRef] [PubMed]

141. Quilez-Molina, A.I.; Merino, D. From Waste to Resource: Methods for Vegetable Waste Transformation into Sustainable Plant-Based Bioplastics. In *Advanced Applications of Biobased Materials: Food, Biomedical, and Environmental Applications*; Elsevier: Amsterdam, The Netherlands, 2023; pp. 61–110. [CrossRef]

142. Sen, K.Y.; Baidurah, S. Renewable Biomass Feedstocks for Production of Sustainable Biodegradable Polymer. *Curr. Opin. Green. Sustain. Chem.* **2021**, *27*, 100412. [CrossRef]

143. Goel, V.; Luthra, P.; Kapur, G.S.; Ramakumar, S.S.V. Biodegradable/Bio-Plastics: Myths and Realities. *J. Polym. Environ.* **2021**, *29*, 3079–3104. [CrossRef]

144. Yrjälä, K.; Ramakrishnan, M.; Salo, E. Agricultural Waste Streams as Resource in Circular Economy for Biochar Production towards Carbon Neutrality. *Curr. Opin. Environ. Sci. Health* **2022**, *26*, 100339. [CrossRef]

145. Asadi Zeidabadi, Z.; Bakhtiari, S.; Abbaslou, H.; Ghanizadeh, A.R. Synthesis, Characterization and Evaluation of Biochar from Agricultural Waste Biomass for Use in Building Materials. *Constr. Build. Mater.* **2018**, *181*, 301–308. [CrossRef]

146. Campos, P.; Miller, A.Z.; Knicker, H.; Costa-Pereira, M.F.; Merino, A.; De la Rosa, J.M. Chemical, Physical and Morphological Properties of Biochars Produced from Agricultural Residues: Implications for Their Use as Soil Amendment. *Waste Manag.* **2020**, *105*, 256–267. [CrossRef] [PubMed]

147. Wijitkosum, S.; Jiwnok, P. Elemental Composition of Biochar Obtained from Agricultural Waste for Soil Amendment and Carbon Sequestration. *Appl. Sci.* **2019**, *9*, 3980. [CrossRef]

148. Pereira Lopes, R.; Astruc, D. Biochar as a Support for Nanocatalysts and Other Reagents: Recent Advances and Applications. *Coord. Chem. Rev.* **2021**, *426*, 213585. [CrossRef]

149. Singh, S.; Kumar Bhaumik, S.; Dong, L.; Li, C.Z.; Vuthaluru, H. An Integrated Two-Step Process of Reforming and Adsorption Using Biochar for Enhanced Tar Removal in Syngas Cleaning. *Fuel* **2022**, *307*, 121935. [CrossRef]

150. Vijay, V.; Shreedhar, S.; Adlak, K.; Payyanad, S.; Sreedharan, V.; Gopi, G.; Sophia van der Voort, T.; Malarvizhi, P.; Yi, S.; Gebert, J.; et al. Review of Large-Scale Biochar Field-Trials for Soil Amendment and the Observed Influences on Crop Yield Variations. *Front. Energy Res.* **2021**, *9*, 710766. [CrossRef]

151. Zhang, Y.; Wang, J.; Feng, Y. The Effects of Biochar Addition on Soil Physicochemical Properties: A Review. *Catena* **2021**, *202*, 105284. [CrossRef]

152. Mansour, M.M.; Soliman, E.; El-Ghamry, A.; El, A.; Kenawy, E.; Biochar, A.M.; Jiang, B.; Mosa, A.; Mansour, M.M.; Soliman, E.; et al. Biochar as a Soil Amendment for Restraining Greenhouse Gases Emission and Improving Soil Carbon Sink: Current Situation and Ways Forward. *Sustainability* **2023**, *15*, 1206. [CrossRef]

153. Qiu, M.; Liu, L.; Ling, Q.; Cai, Y.; Yu, S.; Wang, S.; Fu, D.; Hu, B.; Wang, X. Biochar for the Removal of Contaminants from Soil and Water: A Review. *Biochar* **2022**, *4*, 19. [CrossRef]

154. Liu, M.; Almatrafi, E.; Zhang, Y.; Xu, P.; Song, B.; Zhou, C.; Zeng, G.; Zhu, Y. A Critical Review of Biochar-Based Materials for the Remediation of Heavy Metal Contaminated Environment: Applications and Practical Evaluations. *Sci. Total Environ.* **2022**, *806*, 150531. [CrossRef] [PubMed]

155. Janu, R.; Mrlik, V.; Ribitsch, D.; Hofman, J.; Sedláček, P.; Bielská, L.; Soja, G. Biochar Surface Functional Groups as Affected by Biomass Feedstock, Biochar Composition and Pyrolysis Temperature. *Carbon. Resour. Convers.* **2021**, *4*, 36–46. [CrossRef]

156. Karimi, M.; Shirzad, M.; Silva, J.A.C.; Rodrigues, A.E. Biomass/Biochar Carbon Materials for CO_2 Capture and Sequestration by Cyclic Adsorption Processes: A Review and Prospects for Future Directions. *J. CO2 Util.* **2022**, *57*, 101890. [CrossRef]

157. Yeboah, M.L.; Li, X.; Zhou, S. Facile Fabrication of Biochar from Palm Kernel Shell Waste and Its Novel Application to Magnesium-Based Materials for Hydrogen Storage. *Materials* **2020**, *13*, 625. [CrossRef] [PubMed]

158. Hao, S.; Chen, X.; Wu, H.; Zeng, X.; Dong, P.; Han, L.; Yu, F.; Cai, W.; Xie, Y.; Xiao, J.; et al. A Novel Chinese Parasol Leaf Biochar Fuelled Direct Carbon Solid Oxide Fuel Cell for High Performance Electricity Generation. *Int. J. Hydrog. Energy* **2022**, *47*, 1172–1182. [CrossRef]

159. Song, B.; Wang, Q.; Ali, J.; Wang, Z.; Wang, L.; Wang, J.; Li, J.; Glebov, E.M.; Zhuang, X. Biochar-Supported Fe3C Nanoparticles with Enhanced Interfacial Contact as High-Performance Binder-Free Anode Material for Microbial Fuel Cells. *Chem. Eng. J.* **2023**, *474*, 145678. [CrossRef]

160. Kacprzak, A.; Włodarczyk, R. Utilization of Organic Waste in a Direct Carbon Fuel Cell for Sustainable Electricity Generation. *Energies* **2023**, *16*, 7359. [CrossRef]

161. Patwardhan, S.B.; Pandit, S.; Kumar Gupta, P.; Kumar Jha, N.; Rawat, J.; Joshi, H.C.; Priya, K.; Gupta, M.; Lahiri, D.; Nag, M.; et al. Recent Advances in the Application of Biochar in Microbial Electrochemical Cells. *Fuel* **2022**, *311*, 122501. [CrossRef]

162. Qin, C.; Wang, H.; Yuan, X.; Xiong, T.; Zhang, J.; Zhang, J. Understanding Structure-Performance Correlation of Biochar Materials in Environmental Remediation and Electrochemical Devices. *Chem. Eng. J.* **2020**, *382*, 122977. [CrossRef]

163. Shrivastava, K.; Jain, A. Development of Sustainable High-Performance Supercapacitor Electrodes from Biochar-Based Material. In *Energy Storage Technologies in Grid Modernization*; Wiley: Hoboken, NJ, USA, 2023; pp. 71–104. [CrossRef]

164. Xiang, W.; Zhang, X.; Chen, J.; Zou, W.; He, F.; Hu, X.; Tsang, D.C.W.; Ok, Y.S.; Gao, B. Biochar Technology in Wastewater Treatment: A Critical Review. *Chemosphere* **2020**, *252*, 126539. [CrossRef] [PubMed]

165. He, M.; Zhu, X.; Dutta, S.; Khanal, S.K.; Lee, K.T.; Masek, O.; Tsang, D.C.W. Catalytic Co-Hydrothermal Carbonization of Food Waste Digestate and Yard Waste for Energy Application and Nutrient Recovery. *Bioresour. Technol.* **2022**, *344*, 126395. [CrossRef] [PubMed]

166. Pauline, A.L.; Joseph, K. Hydrothermal Carbonization of Organic Wastes to Carbonaceous Solid Fuel—A Review of Mechanisms and Process Parameters. *Fuel* **2020**, *279*, 118472. [CrossRef]

167. Ischia, G.; Fiori, L. Hydrothermal Carbonization of Organic Waste and Biomass: A Review on Process, Reactor, and Plant Modeling. *Waste Biomass Valorization* **2020**, *12*, 2797–2824. [CrossRef]

168. Aragon-Briceño, C.; Pożarlik, A.; Bramer, E.; Brem, G.; Wang, S.; Wen, Y.; Yang, W.; Pawlak-Kruczek, H.; Niedźwiecki, Ł.; Urbanowska, A.; et al. Integration of Hydrothermal Carbonization Treatment for Water and Energy Recovery from Organic Fraction of Municipal Solid Waste Digestate. *Renew. Energy* **2022**, *184*, 577–591. [CrossRef]

169. Pawlak-Kruczek, H.; Niedzwiecki, L.; Sieradzka, M.; Mlonka-Mędrala, A.; Baranowski, M.; Serafin-Tkaczuk, M.; Magdziarz, A. Hydrothermal Carbonization of Agricultural and Municipal Solid Waste Digestates—Structure and Energetic Properties of the Solid Products. *Fuel* **2020**, *275*, 117837. [CrossRef]

170. Belete, Y.Z.; Mau, V.; Yahav Spitzer, R.; Posmanik, R.; Jassby, D.; Iddya, A.; Kassem, N.; Tester, J.W.; Gross, A. Hydrothermal Carbonization of Anaerobic Digestate and Manure from a Dairy Farm on Energy Recovery and the Fate of Nutrients. *Bioresour. Technol.* **2021**, *333*, 125164. [CrossRef]

171. Naisse, C.; Girardin, C.; Lefevre, R.; Pozzi, A.; Maas, R.; Stark, A.; Rumpel, C. Effect of Physical Weathering on the Carbon Sequestration Potential of Biochars and Hydrochars in Soil. *GCB Bioenergy* **2015**, *7*, 488–496. [CrossRef]

172. Putra, H.E.; Damanhuri, E.; Dewi, K.; Pasek, A.D. Hydrothermal Treatment of Municipal Solid Waste into Coal-like Fuel. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *483*, 012021. [CrossRef]

173. Sharma, H.B.; Sarmah, A.K.; Dubey, B. Hydrothermal Carbonization of Renewable Waste Biomass for Solid Biofuel Production: A Discussion on Process Mechanism, the Influence of Process Parameters, Environmental Performance and Fuel Properties of Hydrochar. *Renew. Sustain. Energy Rev.* **2020**, *123*, 109761. [CrossRef]

174. Mong, G.R.; Tan, H.; Chin Vui Sheng, D.D.; Kek, H.Y.; Nyakuma, B.B.; Woon, K.S.; Othman, M.H.D.; Kang, H.S.; Goh, P.S.; Wong, K.Y. A Review on Plastic Waste Valorisation to Advanced Materials: Solutions and Technologies to Curb Plastic Waste Pollution. *J. Clean. Prod.* **2024**, *434*, 140180. [CrossRef]

175. Zhou, Y.; Remón, J.; Pang, X.; Jiang, Z.; Liu, H.; Ding, W. Hydrothermal Conversion of Biomass to Fuels, Chemicals and Materials: A Review Holistically Connecting Product Properties and Marketable Applications. *Sci. Total Environ.* **2023**, *886*, 163920. [CrossRef]

176. Murillo, H.A.; Pagés-Díaz, J.; Díaz-Robles, L.A.; Vallejo, F.; Huiliñir, C. Valorization of Oat Husk by Hydrothermal Carbonization: Optimization of Process Parameters and Anaerobic Digestion of Spent Liquors. *Bioresour. Technol.* **2022**, *343*, 126112. [CrossRef]

177. Cho, E.J.; Trinh, L.T.P.; Song, Y.; Lee, Y.G.; Bae, H.J. Bioconversion of Biomass Waste into High Value Chemicals. *Bioresour. Technol.* **2020**, *298*, 122386. [CrossRef] [PubMed]

178. Moon, M.; Yeon, Y.J.; Park, H.J.; Park, J.; Park, G.W.; Kim, G.H.; Lee, J.P.; Lee, D.; Lee, J.S.; Min, K. Chemoenzymatic Valorization of Agricultural Wastes into 4-Hydroxyvaleric Acid via Levulinic Acid. *Bioresour. Technol.* **2021**, *337*, 125479. [CrossRef] [PubMed]

179. Global Furfural Market by Raw Material (Sugarcane Bagasse, Corncob, Rice Husk), Application (Derivatives, Solvents), End-use Industry (Agriculture, Paint & Coatings, Pharmaceuticals, Food & Beverages, Refineries), and Region—Forecast to 2028. Available online: https://www.researchandmarkets.com/report/furfural (accessed on 25 March 2024).

180. Tapia-Quirós, P.; Montenegro-Landívar, M.F.; Vecino, X.; Alvarino, T.; Cortina, J.L.; Saurina, J.; Granados, M.; Reig, M. A Green Approach to Phenolic Compounds Recovery from Olive Mill and Winery Wastes. *Sci. Total Environ.* **2022**, *835*, 155552. [CrossRef] [PubMed]

181. Li, S.; Chen, G. Agricultural Waste-Derived Superabsorbent Hydrogels: Preparation, Performance, and Socioeconomic Impacts. *J. Clean. Prod.* **2020**, *251*, 119669. [CrossRef]

182. Al kamzari, S.M.A.; Nageswara Rao, L.; Lakavat, M.; Gandi, S.; Reddy, P.S.; Kavitha Sri, G. Extraction and Characterization of Cellulose from Agricultural Waste Materials. *Mater. Today Proc.* **2023**, *80*, 2740–2743. [CrossRef]

183. Das, D.; Prakash, P.; Rout, P.K.; Bhaladhare, S. Synthesis and Characterization of Superabsorbent Cellulose-Based Hydrogel for Agriculture Application. *Starch–Stärke* **2021**, *73*, 1900284. [CrossRef]

184. Wang, X.; Yao, C.; Wang, F.; Li, Z. Cellulose-Based Nanomaterials for Energy Applications. *Small* **2017**, *13*, 1702240. [CrossRef] [PubMed]

185. Bian, H.; Gao, Y.; Luo, J.; Jiao, L.; Wu, W.; Fang, G.; Dai, H. Lignocellulosic Nanofibrils Produced Using Wheat Straw and Their Pulping Solid Residue: From Agricultural Waste to Cellulose Nanomaterials. *Waste Manag.* **2019**, *91*, 1–8. [CrossRef]

186. Ghalehno, M.D.; Yousefi, H. Green Nanocomposite Made from Carboxymethyl Cellulose Reinforced with Four Types of Cellulose Nanomaterials of Wheat Straw. *J. Appl. Polym. Sci.* **2022**, *139*, e52802. [CrossRef]

187. Thakur, M.; Sharma, A.; Ahlawat, V.; Bhattacharya, M.; Goswami, S. Process Optimization for the Production of Cellulose Nanocrystals from Rice Straw Derived α-Cellulose. *Mater. Sci. Energy Technol.* **2020**, *3*, 328–334. [CrossRef]

188. Hsieh, Y.-L. Cellulose Nanocrystals and Self-Assembled Nanostructures from Cotton, Rice Straw and Grape Skin: A Source Perspective. *J. Mater. Sci.* **2013**, *48*, 7837–7846. [CrossRef]

189. Khoo, R.Z.; Chow, W.S.; Ismail, H. Sugarcane Bagasse Fiber and Its Cellulose Nanocrystals for Polymer Reinforcement and Heavy Metal Adsorbent: A Review. *Cellulose* **2018**, *25*, 4303–4330. [CrossRef]

190. Torgbo, S.; Quan, V.M.; Sukyai, P. Cellulosic Value-Added Products from Sugarcane Bagasse. *Cellulose* **2021**, *28*, 5219–5240. [CrossRef]

191. de Aguiar, J.; Bondancia, T.J.; Claro, P.I.C.; Mattoso, L.H.C.; Farinas, C.S.; Marconcini, J.M. Enzymatic Deconstruction of Sugarcane Bagasse and Straw to Obtain Cellulose Nanomaterials. *ACS Sustain. Chem. Eng.* **2020**, *8*, 2287–2299. [CrossRef]

192. Vu, H.P.; Nguyen, L.N.; Vu, M.T.; Johir, M.A.H.; McLaughlan, R.; Nghiem, L.D. A Comprehensive Review on the Framework to Valorise Lignocellulosic Biomass as Biorefinery Feedstocks. *Sci. Total Environ.* **2020**, *743*, 140630. [CrossRef]

193. Xu, N.; Liu, S.; Xin, F.; Zhou, J.; Jia, H.; Xu, J.; Jiang, M.; Dong, W. Biomethane Production from Lignocellulose: Biomass Recalcitrance and Its Impacts on Anaerobic Digestion. *Front. Bioeng. Biotechnol.* **2019**, *7*, 472405. [CrossRef]

194. Banu, J.R.; Sugitha, S.; Kavitha, S.; Kannah, R.Y.; Merrylin, J.; Kumar, G. Lignocellulosic Biomass Pretreatment for Enhanced Bioenergy Recovery: Effect of Lignocelluloses Recalcitrance and Enhancement Strategies. *Front. Energy Res.* **2021**, *9*, 646057. [CrossRef]

195. Zhu, D.; Wang, Z.; Liu, K.; Si, B.; Yang, G.; Tian, C.; Zhang, Y. Multi-Cycle Anaerobic Digestion of Hydrothermal Liquefaction Aqueous Phase: Role of Carbon and Iron Based Conductive Materials in Inhibitory Compounds Degradation, Microbial Structure Shaping, and Interspecies Electron Transfer Regulation. *Chem. Eng. J.* **2023**, *454*, 140019. [CrossRef]

196. Balasundaram, G.; Banu, R.; Varjani, S.; Kazmi, A.A.; Tyagi, V.K. Recalcitrant Compounds Formation, Their Toxicity, and Mitigation: Key Issues in Biomass Pretreatment and Anaerobic Digestion. *Chemosphere* **2022**, *291*, 132930. [CrossRef]

197. Balu, A.M.; Nuñez, A.G. *Biomass and Biowaste: New Chemical Products from Old. Biomass and Biowaste: New Chemical Products from Old*; De Gruyter: Berlin, Germany, 2020; pp. 1–182.

198. He, O.; Zhang, Y.; Wang, P.; Liu, L.; Wang, Q.; Yang, N.; Li, W.; Champagne, P.; Yu, H. Experimental and Kinetic Study on the Production of Furfural and HMF from Glucose. *Catalysts* **2020**, *11*, 11. [CrossRef]

199. Thakur, A.; Kumar, A.; Kaya, S.; Vo, D.V.N.; Sharma, A. Suppressing Inhibitory Compounds by Nanomaterials for Highly Efficient Biofuel Production: A Review. *Fuel* **2022**, *312*, 122934. [CrossRef]

200. Cousin, E.; Namhaed, K.; Pérès, Y.; Cognet, P.; Delmas, M.; Hermansyah, H.; Gozan, M.; Alaba, P.A.; Aroua, M.K. Towards Efficient and Greener Processes for Furfural Production from Biomass: A Review of the Recent Trends. *Sci. Total Environ.* **2022**, *847*, 157599. [CrossRef] [PubMed]

201. Choudhary, A.; Kumar, V.; Kumar, S.; Majid, I.; Aggarwal, P.; Suri, S. 5-Hydroxymethylfurfural (HMF) Formation, Occurrence and Potential Health Concerns: Recent Developments. *Toxin Rev.* **2021**, *40*, 545–561. [CrossRef]

202. Mohamad Said, K.A.; Ismail, A.F.; Abdul Karim, Z.; Abdullah, M.S.; Hafeez, A. A Review of Technologies for the Phenolic Compounds Recovery and Phenol Removal from Wastewater. *Process Saf. Environ. Prot.* **2021**, *151*, 257–289. [CrossRef]

203. Oliveira, D.M.; Hoshino, É.P.; Mota, T.R.; Marchiosi, R.; Ferrarese-Filho, O.; dos Santos, W.D. Modulation of Cellulase Activity by Lignin-Related Compounds. *Bioresour. Technol. Rep.* **2020**, *10*, 100390. [CrossRef]

204. Valanciene, E.; Jonuskiene, I.; Syrpas, M.; Augustiniene, E.; Matulis, P.; Simonavicius, A.; Malys, N. Advances and Prospects of Phenolic Acids Production, Biorefinery and Analysis. *Biomolecules* **2020**, *10*, 874. [CrossRef] [PubMed]

205. Radhika, N.L.; Sachdeva, S.; Kumar, M. Lignin Depolymerization and Biotransformation to Industrially Important Chemicals/Biofuels. *Fuel* **2022**, *312*, 122935. [CrossRef]

206. van der Maas, L.; Driessen, J.L.S.P.; Mussatto, S.I. Effects of Inhibitory Compounds Present in Lignocellulosic Biomass Hydrolysates on the Growth of Bacillus Subtilis. *Energies* **2021**, *14*, 8419. [CrossRef]

207. Chen, Y.; Yang, Y.; Liu, X.; Shi, X.; Wang, C.; Zhong, H.; Jin, F. Sustainable Production of Formic Acid and Acetic Acid from Biomass. *Mol. Catal.* **2023**, *545*, 113199. [CrossRef]

208. Tan, Z.; Li, X.; Yang, C.; Liu, H.; Cheng, J.J. Inhibition and Disinhibition of 5-Hydroxymethylfurfural in Anaerobic Fermentation: A Review. *Chem. Eng. J.* **2021**, *424*, 130560. [CrossRef]

209. Liu, B.; Liu, L.; Deng, B.; Huang, C.; Zhu, J.; Liang, L.; He, X.; Wei, Y.; Qin, C.; Liang, C.; et al. Application and Prospect of Organic Acid Pretreatment in Lignocellulosic Biomass Separation: A Review. *Int. J. Biol. Macromol.* **2022**, *222*, 1400–1413. [CrossRef] [PubMed]

210. Gao, Z.; Alshehri, K.; Li, Y.; Qian, H.; Sapsford, D.; Cleall, P.; Harbottle, M. Advances in Biological Techniques for Sustainable Lignocellulosic Waste Utilization in Biogas Production. *Renew. Sustain. Energy Rev.* **2022**, *170*, 112995. [CrossRef]

211. Uthirakrishnan, U.; Godvin Sharmila, V.; Merrylin, J.; Adish Kumar, S.; Dharmadhas, J.S.; Varjani, S.; Rajesh Banu, J. Current Advances and Future Outlook on Pretreatment Techniques to Enhance Biosolids Disintegration and Anaerobic Digestion: A Critical Review. *Chemosphere* **2022**, *288*, 132553. [CrossRef]

212. Yang, P.; Peng, Y.; Tan, H.; Liu, H.; Wu, D.; Wang, X.; Li, L.; Peng, X. Foaming Mechanisms and Control Strategies during the Anaerobic Digestion of Organic Waste: A Critical Review. *Sci. Total Environ.* **2021**, *779*, 146531. [CrossRef]

213. Liu, T.; Goux, X.; Calusinska, M.; Westerholm, M. Analyzing Microbial Core Communities, Rare Species, and Interspecies Interactions Can Help Identify Core Microbial Functions in Anaerobic Degradation. In *Assessing the Microbiological Health of Ecosystems*; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2022; pp. 127–157. [CrossRef]

214. Fernández-Sandoval, M.T.; García, A.; Teymennet-Ramírez, K.V.; Arenas-Olivares, D.Y.; Martínez-Morales, F.; Trejo-Hernández, M.R. Removal of Phenolic Inhibitors from Lignocellulose Hydrolysates Using Laccases for the Production of Fuels and Chemicals. *Biotechnol. Prog.* **2023**, *40*, e3406. [CrossRef]

215. Cucina, M.; Pezzolla, D.; Tacconi, C.; Gigliotti, G. Anaerobic Co-Digestion of a Lignocellulosic Residue with Different Organic Wastes: Relationship between Biomethane Yield, Soluble Organic Matter and Process Stability. *Biomass Bioenergy* **2021**, *153*, 106209. [CrossRef]

216. Kumar, V.; Yadav, S.K.; Kumar, J.; Ahluwalia, V. A Critical Review on Current Strategies and Trends Employed for Removal of Inhibitors and Toxic Materials Generated during Biomass Pretreatment. *Bioresour. Technol.* **2020**, *299*, 122633. [CrossRef] [PubMed]

217. Raja Ram, N.; Nikhil, G.N. A Critical Review on Sustainable Biogas Production with Focus on Microbial-Substrate Interactions: Bottlenecks and Breakthroughs. *Bioresour. Technol. Rep.* **2022**, *19*, 101170. [CrossRef]

218. Dedes, G.; Karnaouri, A.; Topakas, E. Novel Routes in Transformation of Lignocellulosic Biomass to Furan Platform Chemicals: From Pretreatment to Enzyme Catalysis. *Catalysts* **2020**, *10*, 743. [CrossRef]

219. Awogbemi, O.; Kallon, D.V. Von Pretreatment Techniques for Agricultural Waste. *Case Stud. Chem. Environ. Eng.* **2022**, *6*, 100229. [CrossRef]

220. Lorenci Woiciechowski, A.; Dalmas Neto, C.J.; Porto de Souza Vandenberghe, L.; de Carvalho Neto, D.P.; Novak Sydney, A.C.; Letti, L.A.J.; Karp, S.G.; Zevallos Torres, L.A.; Soccol, C.R. Lignocellulosic Biomass: Acid and Alkaline Pretreatments and Their Effects on Biomass Recalcitrance—Conventional Processing and Recent Advances. *Bioresour. Technol.* **2020**, *304*, 122848. [CrossRef] [PubMed]

221. Chen, X.; Zhai, R.; Li, Y.; Yuan, X.; Liu, Z.H.; Jin, M. Understanding the Structural Characteristics of Water-Soluble Phenolic Compounds from Four Pretreatments of Corn Stover and Their Inhibitory Effects on Enzymatic Hydrolysis and Fermentation. *Biotechnol. Biofuels* **2020**, *13*, 1–13. [CrossRef]

222. Sheng, Y.; Lam, S.S.; Wu, Y.; Ge, S.; Wu, J.; Cai, L.; Huang, Z.; Van Le, Q.; Sonne, C.; Xia, C. Enzymatic Conversion of Pretreated Lignocellulosic Biomass: A Review on Influence of Structural Changes of Lignin. *Bioresour. Technol.* **2021**, *324*, 124631. [CrossRef]

223. Wu, Z.; Peng, K.; Zhang, Y.; Wang, M.; Yong, C.; Chen, L.; Qu, P.; Huang, H.; Sun, E.; Pan, M. Lignocellulose Dissociation with Biological Pretreatment towards the Biochemical Platform: A Review. *Mater. Today Bio* **2022**, *16*, 100445. [CrossRef]

224. Usman Khan, M.; Kiaer Ahring, B. Improving the Biogas Yield of Manure: Effect of Pretreatment on Anaerobic Digestion of the Recalcitrant Fraction of Manure. *Bioresour. Technol.* **2021**, *321*, 124427. [CrossRef]

225. Zhang, D.; Feng, Y.; Huang, H.; Khunjar, W.; Wang, Z.W. Recalcitrant Dissolved Organic Nitrogen Formation in Thermal Hydrolysis Pretreatment of Municipal Sludge. *Environ. Int.* **2020**, *138*, 105629. [CrossRef] [PubMed]

226. Donkor, K.O.; Gottumukkala, L.D.; Lin, R.; Murphy, J.D. A Perspective on the Combination of Alkali Pre-Treatment with Bioaugmentation to Improve Biogas Production from Lignocellulose Biomass. *Bioresour. Technol.* **2022**, *351*, 126950. [CrossRef] [PubMed]

227. Atiwesh, G.; Parrish, C.C.; Banoub, J.; Le, T.A.T. Lignin Degradation by Microorganisms: A Review. *Biotechnol. Prog.* **2022**, *38*, e3226. [CrossRef] [PubMed]

228. Jiang, Q.; Liu, H.; Zhang, Y.; Cui, M.; Fu, B.; Liu, H. Insight into Sludge Anaerobic Digestion with Granular Activated Carbon Addition: Methanogenic Acceleration and Methane Reduction Relief. *Bioresour. Technol.* **2021**, *319*, 124131. [CrossRef] [PubMed]

229. Diniz, V.; Gasparini Fernandes Cunha, D.; Rath, S. Adsorption of Recalcitrant Contaminants of Emerging Concern onto Activated Carbon: A Laboratory and Pilot-Scale Study. *J. Environ. Manag.* **2023**, *325*, 116489. [CrossRef]

230. Enaime, G.; Baçaoui, A.; Yaacoubi, A.; Lübken, M. Biochar for Wastewater Treatment—Conversion Technologies and Applications. *Appl. Sci.* **2020**, *10*, 3492. [CrossRef]

231. Liu, Z.; Mohseni, M.; Sauvé, S.; Barbeau, B. Segmented Regeneration of Ion Exchange Resins Used for Natural Organic Matter Removal. *Sep. Purif. Technol.* **2022**, *303*, 122271. [CrossRef]

232. Babu Ponnusami, A.; Sinha, S.; Ashokan, H.; Paul, M.V.; Hariharan, S.P.; Arun, J.; Gopinath, K.P.; Hoang Le, Q.; Pugazhendhi, A. Advanced Oxidation Process (AOP) Combined Biological Process for Wastewater Treatment: A Review on Advancements, Feasibility and Practicability of Combined Techniques. *Environ. Res.* **2023**, *237*, 116944. [CrossRef]

233. Pandis, P.K.; Kalogirou, C.; Kanellou, E.; Vaitsis, C.; Savvidou, M.G.; Sourkouni, G.; Zorpas, A.A.; Argirusis, C. Key Points of Advanced Oxidation Processes (AOPs) for Wastewater, Organic Pollutants and Pharmaceutical Waste Treatment: A Mini Review. *ChemEngineering* **2022**, *6*, 8. [CrossRef]

234. Zhang, J.; Kong, C.; Yang, M.; Zang, L. Comparison of Calcium Oxide and Calcium Peroxide Pretreatments of Wheat Straw for Improving Biohydrogen Production. *ACS Omega* **2020**, *5*, 9151–9161. [CrossRef]

235. Zhang, H.; Zhao, J.; Fu, Z.; Wang, Y.; Guan, D.; Xie, J.; Zhang, Q.; Liu, Q.; Wang, D.; Sun, Y. Metagenomic Approach Reveals the Mechanism of Calcium Oxide Improving Kitchen Waste Dry Anaerobic Digestion. *Bioresour. Technol.* **2023**, *387*, 129647. [CrossRef] [PubMed]