

Review

# Lignocellulosic Biorefinery Technologies: A Perception into Recent Advances in Biomass Fractionation, Biorefineries, Economic Hurdles and Market Outlook

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**Abstract:** Lignocellulosic biomasses (LCB) are sustainable and abundantly available feedstocks for the production of biofuel and biochemicals via suitable bioconversion processing. The main aim of this review is to focus on strategies needed for the progression of viable lignocellulosic biomass-based biorefineries (integrated approaches) to generate biofuels and biochemicals. Processing biomass in a sustainable manner is a major challenge that demands the accomplishment of basic requirements relating to cost effectiveness and environmental sustainability. The challenges associated with biomass availability and the bioconversion process have been explained in detail in this review. Limitations associated with biomass structural composition can obstruct the feasibility of biofuel production, especially in mono-process approaches. In such cases, biorefinery approaches and integrated systems certainly lead to improved biofuel conversion. This review paper provides a summary of mono and integrated approaches, their limitations and advantages in LCB bioconversion to biofuel and biochemicals.

**Keywords:** lignocellulosic biomass; fractionation; biorefinery; techno-economic aspect; commercialization



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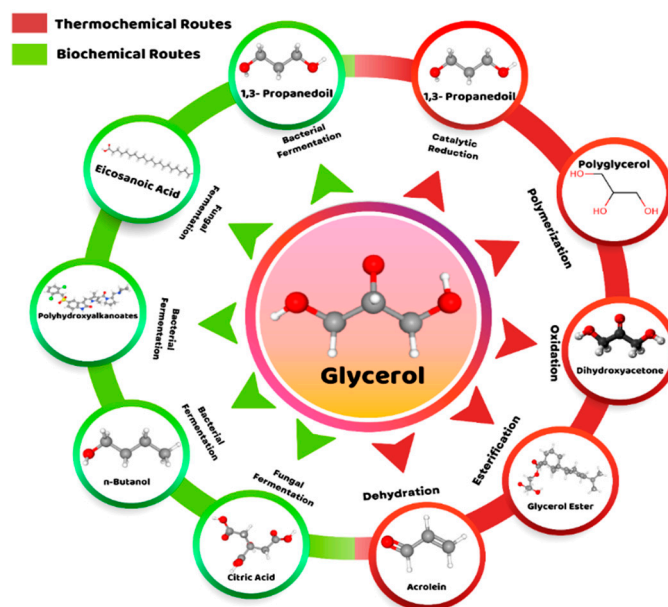
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## 1. Introduction

Rapid growth in industrialization, rising fuel prices, rapid depletion of fossil fuel resources and the increasing rate of greenhouse gas emissions are some of the reasons that compel the need to explore sources for alternate energy and chemicals. In the UN Climate Conference (COP26), climate changes and greenhouse gas emissions were discussed. The current rate of greenhouse gas emissions negatively affects world climate, and, because of global warming, the average temperature rise is higher than 1.5 °C [1]. Traditionally, these chemicals and fuels are obtained from petroleum feedstocks which are non-renewable and usually require a high temperature and high metal catalyst concentration for their operation and processing into the required products [2]. The biomass-based economy has the potential to balance the available energy systems and products that use fossil fuels (e.g., petrochemicals) [3]. The involvement of mild operating conditions, water phase reactions, high reactivity, sustainability and renewable feedstocks make biomass-based chemical methods more advantageous over petrochemical methods. Lignocellulosic biomass, e.g., agricultural and forestry remnants, appears to be advantageous for the generation of various biofuels and biochemicals, including carbon neutral products that are eco-friendly and can be used in various biomedical, bioplastic, food additives pharmaceutical and cosmeceutical industries [3–5]. These biomasses are usually cheap, renewable and abundantly available resources that consist of vital building blocks, such as cellulose, hemicellulose

and lignin, usually in the ranges of 35–55 wt%, 20–40 wt% and 10–25 wt%, respectively. They have the potential to transform into various biofuels, biochemicals and biomaterials, thus offering a substitute for various petroleum-based fuels and chemicals [1,6].

The 'biorefinery' term is derived both from the renewable biomass feedstock and the conversion technologies often applied to treat and process this feedstock to create various products. Fundamentally, it is a sustainable approach where various conversion technologies such as thermochemical, biochemical, chemical processes (Figure 1) and microorganism's growth are integrated to generate multiple high value-added products, chemicals, biofuels and energy [6]. In Figure 1, the green line indicates the biochemical route, and the red color shows the thermochemical routes. The biorefinery concept involves various steps, starting from the selection of suitable feedstock and followed by its pre-treatment to make it more amenable for further processing. Later, it is subjected to various biological and/or chemical treatments to convert them into multiple products. However, the biggest technical and financial hurdles for the lignocellulosic biomass biorefinery include the effective breakdown of the lignocellulose recalcitrance to liberate monomer from the long-chain polymeric sugars and co-utilize lignocellulose components. To tackle this, the feedstock usually undergoes pretreatment processes.



**Figure 1.** Thermochemical and biochemical routes.

Pretreatment is considered an important step in the biomass conversion process as it further affects a majority of other downstream processes such as enzymatic hydrolysis, fermentation and final product separation [7]. Figure 2 represents the various pretreatments involved in the fractionation of lignocellulosic biomass. Physical pretreatments usually require high energy and involve heavy costs compared to other processes. Though chemical pretreatment processes show high selectivity towards the component to be degraded, they usually involve harsh conditions and require a large amount of chemicals which may not be suitable for the biorefinery approach as they may affect other downstream processes. Physicochemical pretreatment usually involves milder chemical conditions but sometimes high temperature and pressure conditions, which generally elevates the cost of biorefinery process [8]. On the other hand, biological processes are more profitable due to limited chemical and energy consumption. However, slow action and very low treatment rates have limited its application.

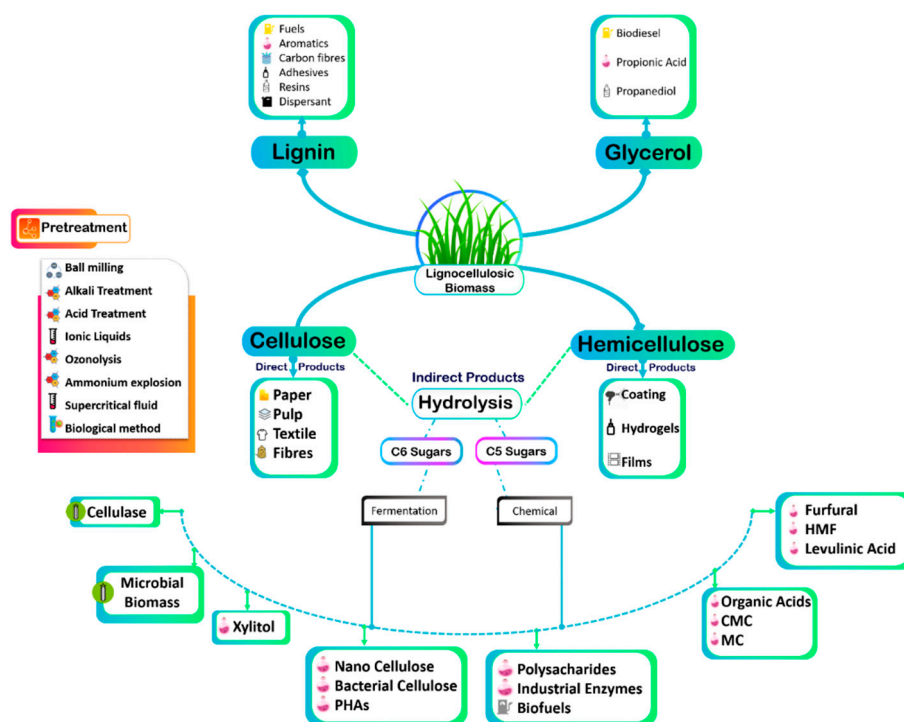


Figure 2. Various pretreatments involved in the fractionation of lignocellulosic biomass.

The biomass conversion is performed through two routes: thermochemical (includes pyrolysis, hydrothermal, liquefaction and gasification) and biochemical (fermentation and anaerobic digestion) [2,6]. However, both have some drawbacks due to which their efficiencies become limited. Thermochemical processes are simple, less selective and less costly compared to biochemical processes because the biochemical processes require necessary pretreatment methods and involve costly enzymes for processing of biomass (Figure 1). So, to overcome the limitations of thermochemical and biochemical processes, an integrated approach should be adopted to increase their efficiencies to maximize the utilization of lignocellulosic biomass. This review provides a comprehensive overview of the concept and technologies involved in lignocellulosic biorefinery, along with the key factors involved in the technoeconomic feasibility of the biorefineries, market outlook and commercialization.

## 2. Fractionation of Biopolymers for Biofuel and Chemicals

Lignocellulosic biomass is composed of polysaccharides that include crystalline polymer cellulose and hemicellulose entangled in linear aromatic polymer lignin with trace quantities of minerals and phenolic substituents that have huge potential for the production of chemicals and fuels [9]. The lignocellulosic biomass represents 90% of the global biomass and is left unused. It is a rich renewable source of carbon and is considered a key resource to meet the demands of a growing population. Despite this, the lignocellulosic biorefinery sector has struggled to become commercially appealing in contrast to traditional biorefinery systems. There are two key challenges with regard to the technological and fundamental components of biorefineries: (i) minimizing waste and energy utilization while effectively using biomass; and (ii) co-production of market-driven products that is flexible.

Lignocellulosic biomass can be potentially exploited through valorization to produce an array of high value-added products. However, the crucial factor that limits complete valorization of the biomass is its compositional structure where cellulose, hemicellulose and lignin are entwined to hinder the penetration or mass transfer of heat or catalysts or enzymes. Further, the high oxygen content of the lignocellulosic biomass reduces the energy density of the biomass and hence necessitates deoxygenation processes. Another important barrier that adds to the difficulty in biological valorization is the recalcitrance

of the lignin polymer and hemicellulose. Pretreatment and fractionation of lignocellulosic biomass can improve the accessibility of the polymers and utilization of every single component of the biomass for efficient conversion into products. The organized crystalline structures are modified during the pretreatment stage, which has an impact on the intrinsic characteristics of the compound bonds found in lignocellulosic materials. Due to this, pretreatment becomes a crucial process by which to enhance the depolymerization of the structural components and effectively improve the conversion to beneficial by-products [10]. However, conventional technologies, such as Kraft, Sulfite and Soda processes, concentrate on transforming biomass into a single component, which comes with the downsides of resource wastage, reduced product value and environmental pollution. Since the main focus is to transform the entire spectrum of lignocellulose into a variety of high-value products and energy sources, a single pretreatment method does not provide the desired biomass degradability that can further improve the efficiency and sustainability of the lignocellulosic biorefinery on both small and large scales. Therefore, combining some of these techniques is required to increase the effectiveness of lignocellulosic pretreatment.

Fractionation is a stepwise transformation technology that ensures the high-value utilization of each component according to the characteristics and dynamic market demand and hence can be used to overcome these aforementioned challenges and the heterogeneity of lignocellulosic biomass [11]. Fractionation combines a variety of pretreatments to separate each component, while also allowing fraction recovery operations with fewer purification stages [12]. An obstacle to establishing a process for simultaneous valorization is presented by the reactive nature of three biopolymers in various biorefinery settings. The efficacy of lignocellulosic fractionation methods validates the criteria: (1) cellulose, hemicellulose and lignin are extracted at a higher yield with minimal degradation for fuel and chemical applications; (2) limited degraded and toxic products; and (3) minimal capital and operational expenses, together with regeneration of chemicals. Some fractionation processes such as dilute acid, alkali, ionic liquid, deep eutectic solvent (DES), hydrothermal, organosolv and other green solvents provide environment-friendly and efficient pathways to separate lignocellulosic biomass into valuable fractions (Table 1); however, they require more intense research to achieve industrialization and generate high-value bioproducts [12].

Acids such as hydrochloric acid, sulfuric acid or nitric acid solubilize the lignin to hydrolyze the cellulose and hemicellulose. Acid treatments are conducted either with concentrated acids or dilute forms in the presence of high temperatures. Wang et al. (2020) investigated a mild one-pot acid-catalyzed pretreatment approach on lignocellulosic biorefinery to achieve 90% lignin, 96% of cellulose and 77% of xylan separation without formation of any deleterious byproducts (e.g., furfural and 5-hydroxymethylfurfural) [13]. Dilute acid involves a significant amount of energy and concentrated acids causes corrosion. Alkalis cleave the ester, aryl-ether and alkyl-aryl linkages to increase the internal surface area, partially crystallize cellulose, dissolve the hemicelluloses and modify the structure of lignin. To overcome the recalcitrance of lignocellulosic biomass, sulfide pre-treatment is used. The sequential application of acid-alkaline treatment has demonstrated a potential to generate lignin with high industrial potential and fermentable sugars and porous cellulosic fibers [14]. Briefly, the acid treatment in the first stage hydrolyzed the lignocellulose to remove hemicellulose, and subsequent exposure to alkali in the second stage produced lignin and cellulose.

**Table 1.** Fractionation of lignocellulosic biomass to monosaccharides and phenolic monomers.

Substrate	Method	Conditions	Monomers	Yield	References
Black liquor	Hydrothermal treatment followed by wet oxidation	115–220 °C and N <sub>2</sub>	Monosaccharide	<73%	[15]
Birch chips	Reductive Catalytic Fractionation	RuN/ZnO/C catalyst and Methanol	Phenolic monomers	46.4 wt% lignin	[16]
Monosaccharide	82 wt% cellulose		Monosaccharide	82 wt% cellulose	
Wheat straw	Hydrothermal Treatment	220 °C	Monosaccharide	43%	[17]
Paulownia wood	Microwave treatment followed by hydrothermal	200–230 °C	Monosaccharide	80%	[18]
Pinewood	Green solvent (Dimethyl Carbonate)	H <sub>2</sub> SO <sub>4</sub> as catalyst; ethylene glycol as stabilizing agent	Phenolic monomers	9 wt%	[19]
			Monosaccharide	84.7%	
Poplar	Acid-Catalyzed Biphasic Water/Phenol System	Acidic water/phenol at 120 °C	Monosaccharide	77%	[13]
Dry olive pomace	Hydrothermal treatment followed by dilute acid	115–220 °C and 1–2% sulfuric acid	Monosaccharide	<85%	[20]
Sawdusts of spruce	Ionic liquids followed by fermentation	1-ethyl-3-methylimidazolium acetate	Monosaccharide	49.3%	[21]
			Ethanol	54.5%	
Sawdusts of oak			Monosaccharide	59.3%	
			Ethanol	53.9%	
Corn Stover				45.8 ± 1.2 wt% lignin	
Switchgrass				41.5 ± 0.9 wt% lignin	
Miscanthus	Reductive Catalytic Fractionation followed by biphasic extraction	5 wt% Ru/C powder and 2 wt% Ru/alumina pellets	Phenolic monomers	43.8 ± 1.0 wt% lignin	[22]
Sugarcane bagasse				33.7 ± 2.4 wt% lignin	
Wheat Straw				20.0 ± 2.2 wt% lignin	
Flax Shave	Reductive Catalytic Fractionation	3 wt% Ru/C and Ethanol	Phenolic monomers	9.5 wt% lignin	[23]
Black liquor solid	Hydrothermal	300 °C	Phenolic monomers	86.7%	[24]
Pine wood	Reductive Catalytic Fractionation	5 wt% Pd/C and Methanol	Phenolic monomers	56.3 wt% lignin	[25]
Eucalyptus grandis	Reductive Catalytic Fractionation followed by FeCl <sub>3</sub> catalysis	10 wt% Pd/C and Methanol	Phenolic monomers	49.8 wt% lignin	[26]
			Monosaccharide	87.9 wt% cellulose	
<i>Miscanthus × giganteus</i>	Deep Eutectic Solvents	Choline chloride/glycerol with heteropoly acids	Monosaccharide	80%	[27]
Black liquor	Hydrothermal treatment followed by alkali	300 °C and alkalis (NaOH, KOH, Na <sub>2</sub> CO <sub>3</sub> and K <sub>2</sub> CO <sub>3</sub> )	Phenolic monomers	22 wt%	[28]
Black locust bark	Reductive Catalytic Fractionation followed by liquid/liquid extraction	Ru/C and Methanol	Phenolic monomers	35.1 wt% lignin	[29]
Bamboo sawdust	Reductive Catalytic Fractionation followed by enzymatic hydrolysis process	Pd/C and Methanol	Phenolic monomers	<32.2 wt% lignin	[30]
			Monosaccharide	<80.6 wt% cellulose	
Birch sawdust	Reductive Catalytic Fractionation	Co/C and Ethanol	Phenolic monomers	34 wt% lignin	[31]
Wheat straw	Organic solvents followed by alkaline treatment and fermentation	Acetone	Phenolic monomers	<16%	[32]
			Ethanol	<71.1%	
Willow ( <i>Salix matsudana cv. Zhuliu</i> )	Deep Eutectic Solvents	Choline chloride to lactic acid (molar ratio 1:2, 1:4, 1:6, 1:8, 1:10, 1:12)	Phenolic monomers	91.8 wt% lignin	[33]
Municipal solid wastes and corn stover (20:80)	Ionic liquids followed by acid hydrolysis	1-Ethyl-3-methylimidazolium chloride and 1-Butyl-3-methylimidazolium chloride with	Phenolic monomers	22%	[34]
			Monosaccharide	51–70%	
<i>Eucalyptus</i>	Ionic liquids followed by fermentation	1-butyl-3-methylimidazolium acetate	Monosaccharide	<42.6%	[35]
Cedar			<42.1%		
Corn Stover	Reductive Catalytic Fractionation	5 wt% Ni/C and Methanol	Phenolic monomers	28–30 wt% lignin	[36]
Wheat straw	Deep Eutectic Solvents	Choline chloride to oxalic acid dihydrate	Phenolic monomers	57.9%	[37]
Corn cob	Mild acid followed by hydrothermal	310 °C	Phenolic monomers	1.26 wt% lignin	[38]
			Monosaccharide	<60.1%	
Switchgrass	Ionic liquids	1-butyl-3-methylimidazolium acetate	Phenolic monomers	<86.6%	[39]
			Monosaccharide	84%	
Wheat straw	Organic solvent followed by acid hydrolysis	50% w/w aqueous EtOH	Phenolic monomers	84%	[40]
			Monosaccharide	86%	
Eucalyptus wood chips	Organic solvent followed by acid catalysis	Methyl isobutyl ketone:methanol:water (25:42:33) with 5% H <sub>3</sub> PO <sub>4</sub>	Phenolic monomers	13.7 wt%	[41]
			Monosaccharide	17.8 wt%	
wheat straw	Sequential acid–alkaline treatment	dilute sulfuric acid (DAP) (0.1–0.75%, v/v) and dilute sodium hydroxide (AKP) (0.25–3%, w/v) with <121 °C and reaction times (5–60 min)	Monosaccharide	78%	[42]

Hydrothermal treatment, also known as hydro thermolysis or autohydrolysis, exploits the liquid water under pressure at high temperatures to alter the lignocellulosic matrix and produce value-added products [42]. Acetyl groups in hemicelluloses interact with water during hydrothermal treatment to synthesize acetic acid. Dissociated acetic acid catalyzes the breakdown of carbohydrates to dissolve the hemicelluloses and alter the lignocellulosic matrix to make cellulose more accessible. Formation of solubilized hemicellulose and a solid fraction of lignin and cellulose increases the amount of xylooligosaccharides and

bioethanol generated from it due to hydrolysis at high temperatures [43]. According to a recent economic study, operating costs rose by 36% with hydrothermal treatment but ethanol output climbed by 51% thereby increasing the yearly revenues by almost USD 5 million where 100 MT/batch capacity considered [44]. Ethanol yields have been boosted by 97.5% as hydrothermal treatment has reduced the ferulic acid crosslinks leading to higher saccharification and xylose, glucose synthesis. Combining hydrothermal with other pre-treatments such as wet oxidation, microwave, dilute acid, alkaline, wet milling and ultrasonic waves has proved to increase the production of value-added products such as phenols, catechol, guaiacol, xylan, lactic acid, uranoic acid and glycolic acid from lignocellulosic biomass [15,18,45].

Organosolv involves using an organic solvent such as methanol, ethanol, tetrahydrofurfuryl alcohol, ethylene glycol and acetone and organic acids (acetylsalicylic, oxalic, salicylic) or bases (sodium hydroxide, lime) to induce biomass disintegration and generate higher-quality lignin through rupturing the bonds connecting the lignin and hemicelluloses to separate the ether and ester connections between carbohydrates and lignin. A minimal concentration of a highly hydrophobic solvent such as 1-butanol or 1-pentanol could result in effective delignification. Solvent mixtures at varying proportions and organic solvents in the presence of catalysts were also explored by research communities to enhance the cellulose and hemicellulose recovery above 80%. Despite being affordable and non-toxic, organic solvents necessitate a high temperature and a longer holding duration to delignify materials efficiently. Organic acids have shown a higher degree of delignification when compared to alcohol-based organosolv. Although the techniques for valorizing lignocellulosic material and subsequent processing of the fraction are constantly improving, the techno-economic evaluation of the organosolv-based biorefinery remains inefficient [46].

Ionic liquids are largely composed of cations and anions with a melting point less than 100 °C. They form inter and/or intra hydrogen bonds, allowing separation of the lignin fraction and improving the accessibility of cellulose at room temperature and pressure without the production of hazardous inhibitors, acidic or alkaline agents [47]. Due to their excellent thermal stability, high polarity, low vapor pressure, low hydrophobicity, high viscosity and enhanced electrochemical stability, these liquids need little energy and may have little or no negative environmental impact. Ionic liquids such as triethylammonium hydrogen sulfate, pyridinium-based ionic liquids and imidazole derivatives have shown effective and repeated lignocellulose fractionation. Additionally, cellulase is irreversibly inactivated in ionic liquids, which significantly lowers the efficiency of biomass conversion and increases expenses. Deep eutectic solvents (DES) are another type of green solvents made up of Lewis acid and base eutectic mixtures containing a wide variety of anionic and cationic species to meet the increasing demand of energy and materials [48]. These solvents feature a precise ratio of hydrogen bond acceptor and donor, which have minimal volatility and great thermal stability. This makes it an affordable, non-toxic and biodegradable substitute for organic solvents and ionic liquids [49,50]. Due to the solvent's high H-bond capacity and polarity, the lignin deconvolve and dissolve the lignocellulosic complex, resulting in a free crystallite of cellulose that can be utilized to produce fuel and chemicals [51]. Lactic acid, one of the hydrogen-bond donors listed above, demonstrates its viability as a DES component for biomass processing. Furthermore, in a single-stage fractionation and delignification procedure, acidic choline chloride, i.e., lactic acid DES, achieved 88% delignification and 50% extraction of lignin pellets [52]. Enzymatic saccharification can be improved by short-time alkaline enhanced aqueous DES pretreatment, ensuring the viability of sustainable biorefinery techniques [53]. Moreover, it was determined that 24 h and 90 °C were the ideal pretreatment temperature and duration. Song et al. (2019) demonstrated that DES containing lactic acid and betaine in a 2:1 ratio eliminated lignin with higher selectivity and allowed enhanced cellulose and hemicellulose extraction at a pretreatment temperature of 140 °C [54].

Reductive catalytic fractionation (RCF) is a fractionation approach that mainly uses woody biomass and herbaceous plants as feedstock, with a polar and protic solvent

(methanol, ethanol), a heterogeneous redox catalyst (ruthenium, palladium, nickel, molybdenum) and a hydrogen source at high temperatures (up to 200 °C). RCF is a two-step procedure that starts by solvolysis biomass to remove lignin fragments and subsequently proceeds to stabilize it by allowing these intermediates to interact with a hydrogen donor over a redox-active catalyst [55]. From an industrial point of view, alcohol/water combinations can be conducive to improving solvent composition, since high water concentrations favor purer cellulose waste, while low water concentrations improve the removal of lignin. In addition to the substrate’s type and the solvent’s composition, the catalyst has a significant impact on efficiency by accelerating the breakdown of C-O and C-C bonds. The highest efficiency is shown by bi-functional catalysts that contain active metal and acidic centers [36]. Irrespective of the type of fractionation method employed, the efficiency is limited by one or the other drawbacks, as elaborated in Section 3.

### 3. Necessity of Fractionation: Advantages and Disadvantages

Table 2 summarizes the advantages and limitations of the different physical, chemical and biological methods.

**Table 2.** Advantages and limitations of Fractionation methods.

Fractionation Methods	Physicochemical	Chemical	Biological
Mode of Action	Breakdown of cell wall components	Removal of lignin and/or hemicellulose increases the accessible surface area of cellulose	Degradation of polysaccharides to subsequent components
Examples	Pyrolysis, Steam explosion, Liquid hot water treatment, Wet oxidation, Ammonia fibre expansion	Acid and Alkaline treatment, Deep eutectic solvents, Organosolv method, Ionic liquid treatment, supercritical fluids	Microbes, Enzymes
Associated costs	High (need for high pressure and temperature)	Medium (need for expensive chemicals such as organosolv, ionic liquid)	Medium (necessitates elaborative setups)
Energy and chemical requirement	High	High	Low
Applicable to diverse biomass	Yes	Yes	Yes
Inhibitors generation	Low	High	Low
Effectiveness of the process	Medium (can be slow)	High	Medium (also, slow)
Environmental, health and safety concerns	Low	High	High

Given the preceding context and the urgency of the moment, various processes have been identified as having the potential to broaden the spectrum of products from different components of lignocellulosic biomass in a biorefinery setting [56–58]. For example, ionic liquid (1- aminoethyl-3-methylimidazolium nitrate), when used to catalyze hydrothermal treatment, can simultaneously create carbon dots and bioethanol from wheat straw [59]. Similarly, alkali acid pretreatment of birch wood biomass and bamboo followed by hydrogenation with ethanol and bifunctional (Pd/C and Ru/C) catalysts yielded hemicellulose (xylose), cellulose and lignin (methoxyphenols) [60,61]. These procedures provide a substantial advantage for large-scale lignocellulosic biorefineries, where the production of high-value products with minimized waste generation are top priorities (Figure 2). The most typical treatment approach that is carried out in recent times is the hydrothermal treatment followed by DES, ionic liquids or alkaline treatment. With DES (ethylene glycol, choline chloride and aluminum trifluoride in the ratio 1:2:0.1) and imidazole, Ma et al. (2021) and Toscan et al. (2019) synergistically pretreated poplar and elephant grass, re-

spectively. Additionally, the combination of hydrothermal-DES was observed to provide good selectivity for lignin removal and resulted in high glucose production with reduced enzyme digestibility [62,63]. According to Toscan et al. (2019), hydrothermal ionic liquid combinative treatment demonstrated greater solvent recovery as compared to others. Despite these technical concepts, the economic (demand for goods, fuel and chemicals; developing bio-based circular economy), environmental (conservation of natural environment and ecosystem) and social factors (increasing employability; sustainable development of regional areas) necessitate additional evaluation for the expansion of biorefineries [63]. Jiraporn et al. (2022)'s studies on combined hydrothermal and mechanical pretreatment on lignocellulosic biomass achieved 0.488 g/g biomass fermentable sugars obtained at 180 °C in liquid hot water pretreatment for 30 min [64] Marttin et al. (2022)'s study indicated that in combined hydrothermal experiment, -ChCl/LA solids shows higher recovery of hemicellulose as well as delignification than hydrothermal and ChCl/LA solids [65].

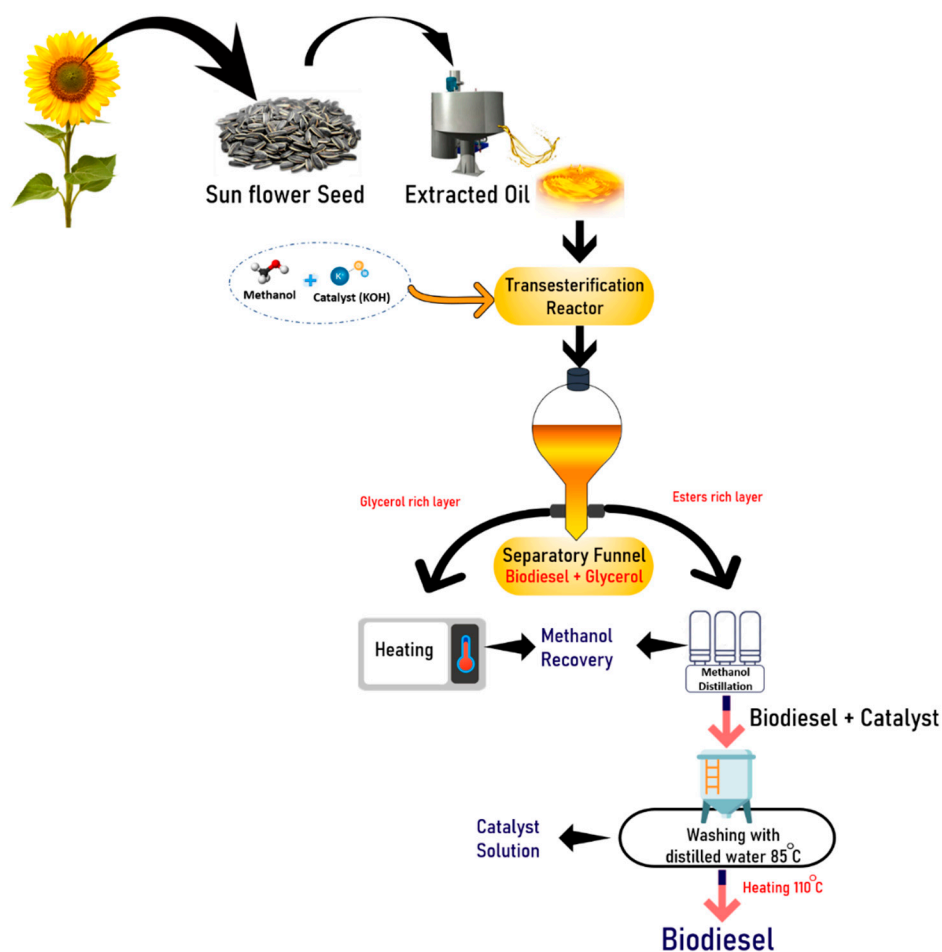
From the economic stand point, combined pre-treatment installations (enzymes, solvents) for producing multiple industrially relevant products can increase the efficiency of the biorefinery. For instance, a biorefinery that processes 1500 dry metric tons (MT) of biomass per day to create high-value products such as xylitol and polyol generates a profit of USD 446 per MT [66]. Although the manufacturing of xylitol and polyol necessitates additional capital expenditure, the economic evaluation demonstrates that their high market values offset the higher capital costs. Similar to this, Zang et al. (2020) suggested one-pot biomass fractionation for the co-production of furfural, lignin and ethanol from lignocellulosic biomass as an inexpensive solution for enterprises [67]. The heightened profitability of the biorefineries in the examples above can be attributed to factors such as reduced waste residues, upcycled solvents and greater aromatic product purity. The use of ethanol and heat integration in the fractionation processes can result in a 5% reduction in energy consumption. Moreover, Kulas et al. (2021) and Rajendran and Murthy (2017) reported that USD 151 million profit per year achieved due to production of carbon fiber, polyurethane foam and activated carbon from lignin conversion [68,69]. Likewise, Kim et al. (2020) improved the economics of tetrahydrofurfuryl alcohol synthesis while using a heating technique that dropped energy demands by 71% [70]. Elliston et al. (2015) also made the important finding that the cost of the multiple feedstock-driven system was decreased with a reduction in the production of inhibitors. Nevertheless, investigations by Rajendran and Murthy (2017) and Bello et al. (2021) brought to light the higher cost of ethanol manufacturing using lignocellulosic biorefinery owing to unpredictability in sugar pricing. Moreover, elevated moisture content in the substrate led to decreasing effectiveness of energy production [69,71]. With respect to environmental sustainability, the foremost advantage offered by the multiple feedstock biorefinery is the decrease in greenhouse gas emissions [69]. According to a recent analysis by Yadav et al. (2021), tannin production had a considerable positive impact on both the economy and the environment, and the use of bioethanol instead of ethanol along with organosolv treatment to fractionate lignocellulosic biomasses lowered the load on GWP. By using spruce bark devoid of tannin as a feedstock, sodium carbonate, sodium bisulfite and energy use were lowered, resulting in decreased manufacturing and environmental costs [72]. Similarly, Kim et al. (2020) concluded that integrating renewable energy sources would boost the sustainability of the biorefinery that produces 2,5-furandicarboxylic acid [70]. Luo et al. (2010) proposed a biorefinery framework that increased eco-efficiency by fixing CO<sub>2</sub> released during ethanol fermentation. However, the presence of agrochemicals and heavy metals in agricultural wastes are the major contributor to human and environmental toxicity. In comparison to agricultural waste, forestry waste has been identified as a viable candidate for modern biorefinery due to the absence of nitrogenous chemicals, which possess the potential to cause eutrophication in adjacent waterbodies [73]. Despite the advantages of lower global warming potential and energy self-sufficient characteristics, optimizing the pretreatment technologies and effective recalcitrance of lignocellulosic biomass restricts the upscaling process. Furthermore, government policies are another crucial factor that



affects the entire process. For instance, the Italian government was the first to promise carbon savings and a 40% reduction in GHG emissions through policies, with the goal of increasing 27% renewable energy capacity by 2030 [74]. Although few studies have been conducted on technoeconomic analysis and almost no studies on the social aspect, each production system is distinct and has advantages and disadvantages that need to be carefully considered [66–68,75,76]. Henceforth, it has not yet been feasible to precisely identify the best technique(s) from an environmental and economic point of view for the production of fuels and platform chemicals. This may be conceivable if more qualitative information becomes available for analysis.

#### 4. Concept of Biorefinery

A biorefinery is a facility or network of facilities that integrates upstream, midstream and downstream processing to turn biomass, including waste, into a spectrum of products such as biochemicals, biofuels, biomaterials and energy. It involves a multi-step process that begins with feed stock selection, processing (pretreatment) and final treatment that includes thermochemical, chemical and biological conversion. Among the various pretreatment procedures (as illustrated in Figure 3), some sophisticated techniques such as supercritical fluids ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and ethanol), ultrasonic irradiation, electromagnetic field perturbation, hydrodynamic cavitation and ionic liquid (IL) pretreatment protocols are identified to be the most effective process for the dissolution and hydrolysis of the biomass components. The prime focus of biorefineries include resource recovery, value addition and waste reduction. The economic dynamics of the biorefinery can be improved by recycling the chemicals and enzymes used as well as by applying methods such as biochar and green solvents (ionic liquids) to remove inhibitors [13].



**Figure 3.** Biodiesel production from sunflower seeds through transesterification reactor.

Different agencies across the globe have defined biorefinery differently, albeit along similar lines. According to the National Renewable Energy Laboratory (NREL), a biorefinery is conceptualized on three different product routes: thermochemical, biochemical and biological (microorganism) platforms. The International Energy Agency (IEA) Bioenergy Task 42 defines biorefinery as “a sustainable process that produces a spectrum of bio-based products (food, feed, chemicals and/or materials) and bioenergy (biofuels, power and/or heat” [77]. In oil-based refineries, crude oil is converted into a variety of energy and chemical products. Likewise, in a product-based biomass biorefinery, biomass is converted into a spectrum of maximum value-added bio-based products and residues that are later combusted for power or heat. At times, the residues subsequent to treatment are considered as precursors or feedstocks for other industries, thus grabbing interest in the economy point of view. Chemicals and materials, high-value low-volume products or specialized chemicals such as cosmetics or nutraceuticals and low-value high-volume products such as transportation fuels (such as biodiesel, bioethanol) are the commodities produced from biorefineries.

Various substrates can be subjected to biorefineries for high value-added product production with no or minimal environmental impacts. Wood, agricultural crops, organic residues (both plant and animal generated), forest wastes and aquatic biomass (algae and sea weeds) are some of the lignocellulosic biomasses that are commonly explored in biorefineries. IEA Bioenergy Task 42 has classified biorefineries on the bases of four categories: feedstocks, processes, platforms and products [77–81].

The biorefineries are categorized into three phases: Phase I biorefineries focus on the production of single product from a single feedstock through a single process or route while Phase II biorefineries produces multiple major products from a single feedstock following multiple processes. Multiple feedstocks involving multiple product production following multiple routes are categorized as Phase III biorefineries. A lignocellulosic biorefinery that produces multiple products such as chemicals, biofuels and bioenergy through multiple conversion routes is an example of a phase III biorefinery. Table 3 summaries the three phases of lignocellulosic biomass biorefineries.

Mono feedstock biorefineries are already functioning around the world and have proven to be beneficial and economically feasible; for instance, many biodiesel-based phase I biorefineries are functional in Europe that are using rapeseed oil to generate biodiesel through a single process of transesterification [82–84]. Figure 3 illustrates biodiesel production from sunflower seeds.

**Table 3.** Lignocellulosic biomass biorefinery (Phase I, II and III).

S. No.	Biorefinery Type	Feedstock	Processes Involved	Final Products	Product Yield	Reference
1	Phase I	Castor oil	Fe <sub>3</sub> O <sub>4</sub> nanoparticles and ethylene glycol in a transesterification process, as an additive.	Biolubricant	94%	[83]
2	Phase I	Prosopis julifera seed	MgO nanocatalyst and ethanol in a transesterification process, as an additive.	Biodiesel	94.83%	[84]
3	Phase I	Castor oil	Catalytic immobilized cation using mussel shell based CaO doped with praseodymium as catalyst (Pr-CaO)	Biodiesel	87.42%	[85]
4	Phase II	birch sawdust (SD)	acidogenic fermentation (AF) and anaerobic digestion	Green hydrogen along with carboxylic acids, biomethane, biohythane	bio H <sub>2</sub> (121.4 mL/gVS), carboxylic acids (0.24 g/g VS), bioCH <sub>4</sub> (246 mL/gVS), biohythane (8–14L)	[86]
5	Phase II	birch wood	catalytic hydrogenolysis (using Pd/C) and hydrothermal processes	phenolic monomers and carbon quantum dots (CQDs)	phenolic monomers (44.6 wt%), CQDs (21.7%)	[87]

**Table 3.** *Cont.*

S. No.	Biorefinery Type	Feedstock	Processes Involved	Final Products	Product Yield	Reference
6	Phase I	Black mustard seed oil	Transesterification using KOH and NaOH as catalyst	Biodiesel	97.34%	[88]
7	Phase I	Rubber oil	base catalyzed transesterification using KOH as catalyst	Biodiesel	98.71%	[89]
8	Phase II	Eucalyptus biomass	reductive catalytic fractionation followed by FeCl <sub>3</sub> catalysis, respectively	Phenolic monomers, 5-hydroxymethylfurfural, levulinic acid and furfural	Phenolic monomers (49.8 wt%)	[90]
9	Phase I	Hiptage benghalensis seed	Transesterification	Biodiesel	~93%	[91]
10	Phase I	Sterculia foetida seed	In-situ acid catalyzed transesterification	Biodiesel	95.91%	[26]
11	Phase I	Sterculia foetida oil	In-situ acid catalyzed transesterification	Biodiesel	91.58%	[26]
12	Phase III	birch wood beech wood corn stalks pine wood	Catalytic Transformation using Pd/C followed by catalytic transfer hydrogenation via Ru/Nb <sub>2</sub> O <sub>5</sub> catalyst and THF/concentrated seawater biphasic system	Furfural, 5-hydroxymethylfurfural, Arenes	-HMF and furfural (upto 24.5 wt%); Arenes (upto 85.6 wt%)	[92]
13	Phase I	Pistacia chinensis seed oil	Catalytic immobilized cation using (GO-SO <sub>3</sub> H/CM@Fe <sub>3</sub> O <sub>4</sub> )	Biodiesel	94%	[93]
14	Phase I	waste cooking oil (WCO)	base catalyzed transesterification using KOH as catalyst	Biodiesel	94%	[94]
15	Phase I	Sterculia foetida oil	Transesterification using KOH as catalyst and ultrasound and infrared techniques	Biodiesel	98.55% (infrared), (99.41%) (ultrasound)	[95]
16	Phase II	Castor plant	Saccharification, Fermentation and Transesterification	Bioethanol and Biodiesel	81.1 g ethanol/kg castor plant, 85% biodiesel	[96]
17	Phase I	Waste cooking oil	Catalytic immobilized cation using CZO nanocomposite	Biodiesel	97.71%	[97]
18	Phase I	waste cooking oil	base catalyzed transesterification using KOH as catalyst	Biodiesel	99.38 wt%	[98]
19	Phase III	Coffee waste Sugarcane Oil palm Banana Rice, corn, cut flowers	Process 1- fermentation of the sugars present in the waste by a thermotolerant mutant Kluyveromyces marxianus Process 2- Conversion of resulting sugar-depleted solids (mostly protein) by Yarrowia lipolytica NRRL YB-567var. Process 3- Conversion of the lignocellulosic fraction of the waste by Saccharomyces cerevisiae NRRL Y-50183 Process 4- anaerobic digestion by Rhodotorulaglutinis NRRL Y-12906 Process 5- pyrocracking processes to produce renewable gasoline and biochar.	Bioethanol, ammonia-fertilizer, Biochemicals, bio-oils, Gasoline	-	[99]
20	Phase III	Waste newspaper + High-density polyethylene	Pyrolysis at heating rate of 20 Cms <sup>-1</sup> and the final temperature from 500–800 °C for 50 s	Alcohols and Hydrocarbons	85.88%	[100]
21	Phase III	Coconut husks + Waste tamarind seeds	Green solvent (deep eutectic solvent composed of choline chloride and oxalic acid dihydrate)	Biodegradable plastics	-	[101]
22	Phase III	Birch wood	Catalytic hydrogenolysis	Carbon Quantum Dots Monomeric phenols	4-propanol guaiacol (10.2 wt%) and 4-propanol syringol (29.7 wt%)	[102]

**Table 3.** *Cont.*

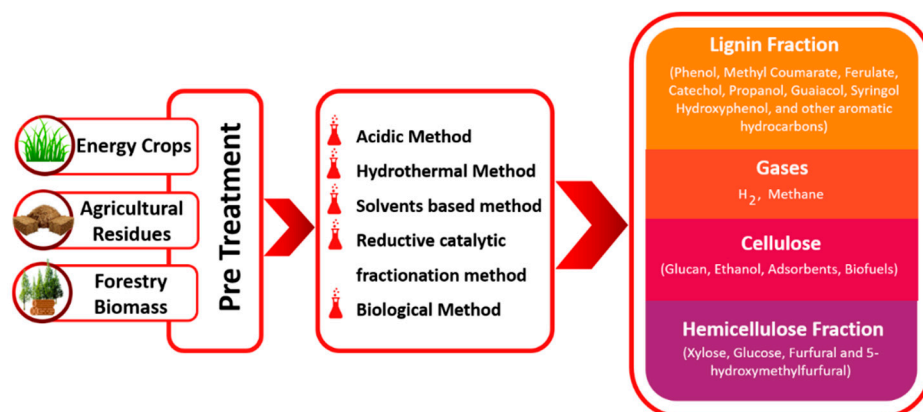
S. No.	Biorefinery Type	Feedstock	Processes Involved	Final Products	Product Yield	Reference
23	Phase III	Wheat straw + Waste polyurethane (PU) plastic	Pyrolysis at a heating rate of 20 Cmin <sup>-1</sup>	Gas (hydrogen, methane, carbondioxide), char and tar	-	[103]
24	Phase III	Bean crop residues + plastic sheets (LDPE) and spent strawberry growing medium + plastic growbags (LDPE)	Slow pyrolysis	Biochar	34–50%	[104]
25	Phase III	Birch sawdust	Organosolv fractionation followed by acidogenic conversion and anerobic fermentation	Biohydrogen	71%	[86]
				Biomethane	78–84%	
				Biohythane, carboxylic acids	-	
26	Phase III	Agricultural waste	Acidogenic fermentation followed by anaerobic digestion	Biogas, fertilizers, compost, polyhydroxyalkanoates and volatile fatty acids	-	[105]
27	Phase III	Corn strover	Heat intergration followed by fermentation	Biodiesel, Bioglycerol	-	[106]
28	Phase III	Bamboo biomass	Hydrothermal and steam explosion treatment followed by fermentation	Biohydrogen	34.20%	[107]
29	Phase III	Wwheat bran + Sago waste + Rice bran	Fermentation using <i>Bacillus</i> sp. PM06	Bioethanol Multiple enzymes, acetic acid	27.67%	[108]
30	Phase III	Residual Cardoon	Steam explosion	Enzymes, Biogas and 1,4-butanediol	-	[109]
31	Phase III	<i>Eucalyptus</i> sawdust	Reductive catalytic fractionation	Phenolics	26.4–49.8%	[110]
				Levulinic acid	73.60%	
				Furfural	55.90%	
32	Phase	Almond shell waste stream	Organosolv fractionation using ethanol/water (70/30 v/v)	Phenolic alcohols	-	[111]
33	Phase III	Grass biomass	Alklaine treatment using 1 wt% NaOH	Hydroxycinnamates, pcoumaric acid ferulic acid	-	[26]

**4.1. Diverse Feedstocks, Multiple Processes and Multiple Products**

This section contrasts with the earlier ones and discusses the most developed and sophisticated form of biorefinery: with numerous feedstocks and products. The development of these biorefineries necessitates the employment of many processes, which are utilized to anticipate cost reductions by sharing energy and materials among processes rather than running separately. Biomass from forestry and agriculture is hydrolyzed to produce value-added products such furans, glycerol, carboxylic acids (levulinic, glutamic, succinic), xylitol, sorbitol, ethanol, 1,4 butanediol and trans-β-Farnesene [112]. Utilizing organic solvents for the lignocellulosic biomass has demonstrated to be a promising method for producing cellulose and chitosan-based materials (also referred as bioadsorbents) for use in waste water treatment and healthcare, in addition to chemicals such as carboxylic acids and biofuels (e.g., hydrogen, methane) for industrial advances [88]. In terms of biological pretreatments, multiple feedstocks subjected to micro-organisms can effectively produce more ethanol, saving up to 25% of total logistics costs and providing resiliency against abnormally low biomass yields [113]. However, the use of enzymes well-suited for polysaccharide contents for different substances might result in greater manufacturing costs. The Supply Characterization Model (SCM) used by Sharma et al. (2020) for multi-feedstock bioenergy production exemplifies the use of the predominant feedstock material (predominantly agricultural and forestry wastes) in the neighboring territory to reduce transport costs and storage concerns [114]. Along with the conventional by-products, Chen et al. (2021) used an innovative cascade biorefinery technique in which softwood biomass

was transformed into quantum dots and used to detect Fe<sup>3+</sup> ions through the integration of catalytic hydrogenolysis and hydrothermal treatment [89]. Likewise, De et al. (2021) successfully created bioplastic film using tamarind seeds and coconut husks using deep eutectic solvent made of fluoride and oxalic acid dihydrate [103]. Conversely, compared to single feedstocks, diverse lignocellulosic materials have a greater level of contamination [115]. Using a variety of feedstocks and pretreatment techniques together can produce commercially significant chemicals and biofuels while lowering the carbon footprint by minimizing waste and byproduct production. Hence, the multi-product biorefinery is efficient in meeting the needs of the current society, i.e., (1) the depletion of petroleum supplies, (2) issues about climate change and (3) conflicts with energy security. Further, product diversity provides a high degree of versatility to meet the rapidly shifting demands while providing multiple alternatives to biorefineries to enhance revenue generation [116].

Pyrgakis and Kokossis (2019) demonstrated annual energy cost and biorefinery profitability in two real-life biorefinery plants in central Europe (Hungary). The first model of biorefinery involved wheat straw and barley as substrates [117]. Winter season was operated with barley, spring with a mixture of wheat and barley and summer and autumn with wheat, resulting in 6.5% of energy savings, decreasing annual energy cost by 11.12 M EUR and earning net profit of 20.054 M /yr. The second biorefinery model, which used wheat and barley in the winter, rice in the summer and miscanthus in the spring, earned a net profit of 6.043–20.169 M/yr. Thus, on comparing these two biorefinery setups, first model utilizing a blend of barley and wheat resulted in the production of bioproducts (xylitol, nylon, poly-urethanes) and biofuels (iso-propanol, butanol). Similarly, Engelberth (2020) emphasized that valorizing food waste containing heterogenous components could be an economical choice in addition to reducing the environmental problems from landfills. Moreover, if a biorefinery is collocated next to a food processing facility in a certain municipality, the problem regarding plant capacity can largely be eliminated. Henceforth, the availability of multi-feedstock enables biorefinery systems to guarantee continuous feedstock supply [118]. Another parameter affecting the economic sensitivity of the multiple-substrates driven biorefinery, according to Ashraf and Schmidt (2018), is the cost of the enzymes and the feed utilized. Bermuda grass, jasmine hedges and date palm in the ratio of 2:2:1 after being subjected to combined hydrothermal and fermentation treatment, produced the least amount of operating expense and 0.53 MW of power generation [119]. An additional potential benefit indicated by the authors was steady supply of substrate in arid and semi-arid regions, where availability of a single substrate is restricted. From a variety of agricultural wastes and woody biomass, pre-treatment techniques such as hydrothermal, green solvent, reductive catalytic fractionation and biological methods have been used to produce biofuel and several useful platform chemicals, including arenes, 5-hydroxymethylfurfural (HMF), volatile fatty acids and furfural. However, there are few studies on the multiple feedstock/multiple products biorefinery. Figure 4 represents the multiple feedstock/products biorefinery.



**Figure 4.** Feedstocks/products biorefinery with various pretreatments.

Through hydrothermal pre-treatment (200 °C for 10 min) and enzymatic hydrolysis (cellulose enzyme), date palm fronds, jasmine hedges and Bermuda grass were successively separated, resulting mostly in monomeric sugars at highly reduced cost of 0.59 USD/kg [119]. When compared to conventional procedures, the minimum selling price of the sugars produced was significantly higher, and the probable reason could be the reduced efficiency of hydrothermal process to fractionate the lignocellulosic components or the on-site treatment of waste effluent. The research mentioned above thus supports the use of residual biomass from forestry and agriculture to offset the cost of the substrate. In a study by Berchem et al. (2020), a combination of feedstocks subjected to alkaline treatment resulted in slightly higher cellulose contamination than single feedstock pretreatments [120]. Additionally, higher-grade lignin was obtained by reducing protein and hemicellulose contamination. Woody biomass was effectively segregated into cellulose fibers, fermentable hemicellulose sugars and lignin employing complete and mild-condition treatments rather than energy-intensive techniques. Lignin-derivable phenol-4-sulfonic acid (PSA) was identified to have the potential to create a “closed-loop” fractionation process, where it serves as a mesoscale solvent to solubilize and preserve lignin fragments in addition to catalyzing the depolymerization process. Another green solvent  $\gamma$ -valerolactone successfully separated the lignocellulosic biomass and improved downstream processing [57]. Additionally, the method may manufacture valerolactone from biomass to make up for the losses and use the evaporation stage to recover the wasted solvent, creating a closed-loop system. According to the techno-economic study, the technology is viable for investment despite the initial high risk involved as the process’s overall income is around USD 500 per MT of dry biomass and has an internal rate of return (IRR) of more than 30%. According to Meramo-Hurtado et al. (2020), the multi-feedstock biorefinery produces positive economic results with a sustainability-weighted return on investment metric (SWROIM) of 27.3% [121]. The biggest practical restriction of the biorefinery systems is the optimization of the processes, despite the huge prospects for advancement.

#### 4.2. Nanotechnology and Lignocellulosic Biorefineries

The intricacy of lignocellulose as a polymeric substance necessitates the need for its breakdown into small monomers, known as platform molecules. Traditional pre-treatment methods result in the production of hazardous substances. Nanoparticles can overcome the drawbacks and improve the pretreatment process by assisting the enzymes to easily penetrate the membrane of the biomass and facilitate the degradation of the substrate bond to release glucose. Nanoparticles also provide stability to work efficiently at higher temperature [122]. For instance, biomass, when pretreated using protease-associated magnesium nanoparticles (MgNPs) at 95 °C, produced more amino acids and removed more lignin as compared to cellulase. Moreover, some nanoparticles, especially magnetic nanoparticles, can be reused and recycled for indefinite periods by applying high magnetic field conditions, thus making lignocellulosic biomass treatment processes more cost-effective. Recently, nanotechnology has made it possible to mobilize enzymes for use in a wide range of applications. Immobilizing enzymes on nanomaterials is a novel strategy to increase enzyme catalytic efficiency. For instance, cellulase mobilized on magnetic nanoparticles was utilized to hydrolyze *Sesbania aculeate* biomass to yield bioethanol of 5.3 gL<sup>-1</sup> [123]. To accomplish effective Avicel hydrolysis, cellulase immobilized on Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles using carbodiimide polymer increased the cellulase activity by 50% [124]. Immobilization favored reuse of the cellulase by at least six times. Moreover, it has been found that biomass pretreated or hydrolyzed with nanoparticles increases the production of end products. Wheat straw that had been treated with silica-cobalt ferrite nanoparticles functionalized with perfluoroalkyl sulfonic and alkyl sulfonic acid produced 46% more sugar. Compared to traditional biohydrogen production, metal oxide nanoparticles resulted in 4.5-fold increase [125]. Employment of nanotechnology in lignocellulosic biorefineries will not only increase the efficiency of pretreatment and hydrolysis steps but

also results in the cost-effectiveness of overall biorefining processes. However, very little research has been conducted to date with nanocatalysts in lignocellulosic biorefineries.

## 5. Key Factors Involved in Techno Economic Aspects of Biorefinery

### 5.1. Availability of Feedstocks

The predominant source of Lignocellulosic biomasses is rice straw, wheat straw, barley straw, wood, coconut husk, sugarcane bagasse, corn stover and sorghum stalks. In India, around 200 million tons of agricultural waste are generated annually, based on a 2017 study [126]. Lignocellulosic biomass production rate is approximately 200 million tons per year and according to the Department of Energy; 1.3 billion dry tons of lignocellulosic biomass are generated yearly in USA alone [126,127]. The perennial herbaceous plant is the main Lignocellulosic biomass, and forest and agricultural residues are other sources [128,129]. Lignocellulose harmonizes with plant cells which contain cellulose, hemicellulose and aromatic polymer lignin. It also has less quantity of inorganic compounds, extractives, proteins and pectin [130]. These compounds are indivisible to form a complex structure [131]. In total lignocellulosic, 30–50% is covered by cellulose; feedstock dry matter lignin consists of 20–40%, which provides structural rigidity, and 15–25% is covered by hemicellulose [128,132]. The 1-4- $\beta$  glycosidic bonds build cellulose fragments with glucopyranosyl monomeric, making crystalline fibrils as a flat structure [131,133]. Among lignocellulosic polymers, cellulose has the highest degree of polymerization. Cellulose makes it low flexibility and insoluble to solvents, whereas hemicellulose has less polymerization than cellulose, which contains glucuronic, methyl, cinnamic, acetyl and galacturonic as functional groups [130,132]. Sugarcane and sugar beets are used for bioethanol production as they contain sucrose, compared with starch and lignocellulosic biomass. Sugar extracts do not require pre-processing before fermentation and have higher biofuel production efficiency [133]. Sugarcane lignocellulosic residues and their dry matter yield have higher biorefinery potential. Lignocellulosic is derived from sugar refinery used for biofuel production [134]. Sweet sorghum stalk is another feedstock used, the juice of which contains fermentable sugars yet has lesser sugar comparable with sugarcane and sugar beets [135,136]. Corn contains starch used for bioethanol production. Corn kernels have 72% the dry weight as starch, the leading source of bioethanol production [137]. Wheat is also contained starch, used for bioethanol production. Other available cereal crops produce less efficient biorefinery, due to low digestibility, as well as phenolic contaminants [138]. Tuber crops and root crops are other feedstocks used for bioethanol production. Similarly, *Manihot esculenta* and sweet potato have a higher starch content and use lesser land for production, which is used for bioethanol production [139,140]. Perennial herbaceous crops produce higher production yields and fewer agricultural requirements [81]. Tall perennial grasses such as switchgrass, reed canary grass, miscanthus and giant reeds can also be used as feedstock. *M. sinensis* and *M. sacchariflorus* have higher water/nitrogen efficiency and tolerance to cold, making stressless cultivation a better choice [141]. Willow and poplar lignocellulosic biomass can be used for biofuel production with higher productivity and short rotation woody crops. These have a higher lignin content of up to 40%, which, as a downside, require effective pretreatment compared to other sources; whereas lower pentose content is marked as a positive side for better fermentation and easy transportation, due to higher biomass density [142]. In Canada, forestry residues are used as the primary source of lignocellulosic biomass; up to 30% of the residue is used during the Roundwood harvesting period. Miscanthus, poplar and switchgrass are the primary lignocellulosic feedstocks in the USA [143]. The following subsections explain, in detail, the key factors that direct the economic feasibility of the lignocellulosic biomass biorefinery (Figure 4).

### 5.2. Conveyance

The cost of biofuel production is a significant challenge in transporting raw materials to the processing plant because of the difficulty in transporting them. Conveyance cost is the summation of fixed as well as variable costs. In trucking, fixed costs include loading

and unloading costs, insurance, depreciation and administrative costs. Variable cost includes fuel and other costs such as repair, tires, lubrication and labor based on distance or location [144]. Equipment used during the process also increases the conveyance charge as machinery rental varies from location to location. The size of the farms and quantity handling also affects the cost, for example, through wages and administrative costs. The biomass supply chain includes unit operation, which depends on the types of biomasses, biorefinery technology and storage techniques employed [145]. The supply chain of the biomass process includes assembly, transportation, storage and processing. Dehydrating, shredding, compaction, pelleting and densification are used as biomass processing technic. Feedstock availability throughout the year is essential for commercialization based on availability, feedstock management and conveyance. Studies denote that half of the cost goes to production, processing and transportation [143]. Conveyance will increase while the biorefinery plant is distant from the collection site, drastically increasing production costs yearly. Thus, the development of an effective logistics plan is essential. Properties such as texture difference, seasonal availability, bulk density and distribution of biomass affect transportation costs [146]. Biomass contains low density, requires more volume and affects the transportation costs. For example, when compared with green crops, corn has 15 times higher bulk density, which directly affects the cost of transportation [76].

Similarly, moisture content also directly affects transportation costs. Transportation of biomass can be conducted in different sizes, such as loose, chopped, baled and pelleted. The requirement of processing dramatically depends on the density of biomass [147,148]. In the USA, more than 90% of feedstock transportation is carried out via trucks and rails, and ships are another means of transportation. A specially modified truck is used in transportation to make logistics cost-effective. For example, tractor-trailers carry nearly nine metric tons of feedstock, which is higher than standard trucks [76]. Searcy et al. (2007) elaborate conveyance cost of feedstock through rail, truck and ship and found 0.01, 0.017 and 0.07 USD /ton/km, respectively. While the ship has a lower transporting cost, loading and unloading cost increases the total cost [144].

### 5.3. Downstream Processing Cost

Downstream processing denotes the process which converts biological components into a homogeneous end product. The downstream process for post-fermentation of lignocellulose biorefinery proceeds through crystallization, concentration, expurgation and distillation. The end product from the process is used on boilers for energy generation as it has a higher energy density [149]. Process integration, along with conversion techniques, makes the approach sustainable. Downstream processing cost for the monotype of feedstock is higher than combined stocks. Thus, using two feedstocks with mixed chemical compositions costs less and makes the overall process eco-friendly. Studies show that 20% or less of lignocellulosic biomass is only digested during the native form. Thus, combining multi-biomass enhances the downstream process [126]. Formic acid is one of the forms of carboxylic acid. Catalytic hydrothermal reactions convert formic acid into Carbon dioxide and hydrogen. So, instead of storing hydrogen, formic acid can be stored, which can be easily converted to hydrogen when needed and makes storage easier. Acetic acid is another carboxylic acid form used as vinegar. Levulinic acid is a by-product used in the pharma and polymer production industries and used as an add-on compound in petrol, whereas levulinic acid is produced quickly from lignocellulosic biomass [150]. Sugar alcohols are another by-product produced in the downstream process of lignocellulosic biomass, typically used in food industries. Thus, downstream processing of the lignocellulosic biomass effectively produces value-added chemicals at the lowest production cost [150].

### 5.4. Scale Up Obstructions and Hurdles

Scaling up from the laboratory model to the plant presents several challenges. Scale-up plants need large quantities of biomass, which need proper management and processing systems. It also requires purification and recovery technic [151]. Various risk factors will



arise while scaling up that need to be identified, and solutions need to be determined, which include the pilot scale, the modeling of the process, flow sheets, cost analysis and product life cycle assessment. Determining which risk factors are essential and need to be considered is crucial [152]. Capital investment is the main component of the scale-up process; further biomass handling and processing must be ported into the industrial scenario. Capital investment must be correctly estimated. KiOR Inc.'s technology scaled up biomass to fuel via thermal conversion to an estimated goal of 500 t/day but could not produce the required quantity due to its structural design problems [143].

Wood processing reduced leads to a fall in production to 10 t/day. Another hurdle reported in Metabolix and ADM involved the production of bioplastic from agricultural lignocellulosic biomass. The primary failure occurred due to precariousness in estimated production and initial cost. When capital cost was lost, this, combined with market adoption, led to the project failure [153]. These indicate the requirements of process amelioration and evolution for successful scale-ups. Microbial factories' scaling process is much more complicated than chemical-based factories. Studies show that chemical processes adopted by biorefineries produce higher by-products than biological processes, which indirectly increases the total cost of the process due to the higher impact on the environment. Thus, the lignocellulosic scaling-up process needs to adhere to points such as deep learning on process integrations and gaps and risk assessment [143]. The management techniques of cell and steel industries with governmental laws make a path for innovations in biorefinery [153]. To catch up with the global need for bioproducts, we require needs up to a 4% growth rate, yet evolving from pilot scale to accurate scale is challenging. Choi et al. (2015)'s studies show the essential compounds of chemicals and their by-products based on commercialization. Studies also show possible challenges during scale-up and the possible additional steps required. The biomass processing upgrade is mainly based on coalescing [154]. Before the scale-up process, extensive studies need to be conducted on the pilot plants, reducing failure risk during scale-up production and providing a deep understanding of various parameters such as design, conveyance and operating facility to reduce the capital.

## 6. Commercialization and Market Outlook

Feedstock selection and processes mainly depend on product yield and energy requirements. Based on the feedstocks, the lignocellulosic biorefinery needs to be analyzed. The total cost of the process includes capital investment, operational cost and feedstock cost. Chandra et al. (2012) researched lignocellulosic agricultural/forestry biomass-based methane and ethanol production and found an energy ratio of 0.83, 0.95, 1.07 and 1.15 for Sugarcane, rice, wheat and maize, respectively [155]. A study suggested that the ethanol production energy ratio improved by adopting anaerobic digestion; meanwhile, ethanol produced from biomass (i.e., lignocellulosic) is more energy-consuming than methane fermentation. During the production process, up to 10 MJ of energy is consumed to produce of 1 L of bioethanol [126]. Lignocellulosic biomass-based biofuel-producing industries evolved dramatically. Various projects have been initiated for advanced biofuel production throughout the world; on the other hand, some plants cannot proceed due to high capital costs [156–165]. Further detailed research is needed for less capital and less running cost. Governments provide subsidies and tax relations to boost this sector. Studies also denote possible ways to make this process cost-effective. Rodrigues Gurgel da Silva et al. (2019) assessed various pretreatment for economic effects while producing biofuel from corn stover [166]. Albashabsheh and Heier Stamm (2019) utilizes mobile pelleting machines to increase biomass supply and study various parameters that affect the overall cost, such as biomass price, conveyance charge, land usage or cost for storage. Based on this report, ethanol production cost from sugarcane bagasse is calculated as USD 1.77 per Litre [167]. Zhao et al. (2015) use acid pretreatment with enzymatic hydrolysis for corn stover to produce bioethanol which costs of 6.05USD / gal, which are higher than the fossil fuels available in the market; thus, additional government subsidies are required for this green

process [168]. Studies in the laboratory and pilot-scale based lignocellulosic biorefinery show promising commercialization [148]. The lignocellulose biorefinery process includes various steps and costs which can be reduced by effective process integration, such as efficient pretreatment and enzymatic process with high enzymatic activity to convert hemicellulose and cellulose into monomeric sugars [164]. Furthermore, we note the use of pentose and hexose sugars with the microbes to produce biofuel. Based on the literature, 40% of the overall production cost is covered by pretreatment [147,169]. Thus, optimizing conditions improve process efficiency as well as reduces production cost. Enzymatic hydrolysis covers 25% of the production cost; optimization further completes it. During the process, various co-product would be generated, which also positively boosts process revenue and make the process waste free [170]. Sabaini et al. (2018) study guayule bagasse-based biofuel production and evaluate the economic possibility with SimSci Pro II. The report suggests that by utilizing co-products, plant size can be increased economically as biomass availability is less, which increases selling [171]. Sindhu et al. (2016) reported that the pretreatment cost covers 40% of the overall processing cost, and Searcy et al. (2007)'s studies show that 50% of the overall processing cost includes accumulation, pre-treating, conveyance and storage [144,169]. Thus, the remaining half of the cost includes energy requirements, running costs for pretreatment and chemical requirements. Another cost that needs to be taken into account is the labor cost as well as an initial investment. Nunes et al. (2020) demonstrated that combining different a source of biomass would reduce the overall cost by 20% [172]. Rocha-Martin et al. (2017) studied the cost of enzymatic saccharification, which required 20% of the overall processing cost, yet it improved the process yield, which would be compensated or improved [170]. Thus, the collection and hydrolysate production required 65% of the overall processing cost, and fermentation, waste treatment and downstream processing covered the remaining 35% of the cost [173]. The commercialization of biorefinery lignocellulosic receives the spotlight as some of the commercial plants for the refinery have production restrictions for the process where lignocellulosic biomass fills the gap. BIOeCON and Khosla jointly started KiOR a thermochemical lignocellulosic biorefinery plant since 2012 [174]. Similarly, several lignocellulose based biorefineries such as Abengoa, Beta Renewables, DuPont, Granbio and Poet-DSM operate with different pretreatment methods to produce renewable fuels, commodities and fine chemicals [175]. The main challenges include logistics, the pretreatment process and farmer participation, which need to be improved.

## 7. Conclusions

The availability of lignocellulosic biomass in the contexts of bioeconomy by the biorefinery was assessed. The initial stage of biorefinery, focussing on energy production, extends to bioproduct production, including chemicals. The properties of lignocellulose added a layer of complexity to achieving full-scale commercial outcomes, and research has been conducted to overcome the hurdles in pretreatment and enzymatic hydrolysis. The fractionation of the biomass is one such specific development of accessible, eco-friendly and profitable pretreatment which qualitatively extracts and separates lignocellulose constituents, thus making the products marketable. Subsequently, site-selection, biomass availability, types, cost for transportation, infrastructure, equipment, maintenance, labor, chemical, energy and disposal affect the economic feasibility of the process. Henceforth, techno-economic life cycle evaluation will aid in determining process and supply chain activities to investigate the significant environmental effects. Governmental subsidies and research on effective process management accelerates commercialization. So far, published work has addressed individual problems rather than establishing a single model, including multivariate analysis. Therefore, such comprehensive analyses would potentially be able to anticipate future environmental and economic implications during the scaling up process.

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