



Advances in Valorization of Lignocellulosic Biomass towards Energy Generation

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Abstract: The booming demand for energy across the world, especially for petroleum-based fuels, has led to the search for a long-term solution as a perfect source of sustainable energy. Lignocellulosic biomass resolves this obstacle as it is a readily available, inexpensive, and renewable fuel source that fulfills the criteria of sustainability. Valorization of lignocellulosic biomass and its components into value-added products maximizes the energy output and promotes the approach of lignocellulosic biorefinery. However, disruption of the recalcitrant structure of lignocellulosic biomass (LCB) via pretreatment technologies is costly and power-/heat-consuming. Therefore, devising an effective pretreatment method is a challenge. Likewise, the thermochemical and biological lignocellulosic conversion poses problems of efficiency, operational costs, and energy consumption. The advent of integrated technologies would probably resolve this problem. However, it is yet to be explored how to make it applicable at a commercial scale. This article will concisely review basic concepts of lignocellulosic composition and the routes opted by them to produce bioenergy. Moreover, it will also discuss the pros and cons of the pretreatment and conversion methods of lignocellulosic biomass. This critical analysis will bring to light the solutions for efficient and cost-effective conversion of lignocellulosic biomass that would pave the way for the development of sustainable energy systems.

Keywords: lignocellulosic biomass; pretreatment; renewable energy; biofuel; biorefinery

1. Introduction

Burgeoning industrialization has surged energy demand, which has augmented the insistence on using petroleum-based fuels. However, they belong to non-renewable sources that have extortionate costs. Production of sustainable energy is a requisite since power plays an imperative role in the development of the economy, social improvements, and humans [1]. The utilization of renewable energy is crucial as it ensures environmental sustainability, energy, and economic security. The shift from petroleum-based materials to



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). biomass-based materials promotes the supply of sustainable carbon feedstock [2]. Lignocellulosic biomass is cellulose-based biomass that is inexpensive and is readily available for energy production. Prime sources of lignocellulosic biomass include agricultural residues, energy crops, forest residues, and cellulosic wastes.

The annual production of lignocellulosic biomass across the world is 181.5 billion tons [3]. An estimated cost of this biomass ranges from USD 24 to USD 121 per ton depending upon the crop, yield, region, and method of analysis [4]. On the contrary, the USA produces 1.3 billion tons of dry biomass annually at the cost of USD 60 to generate bioenergy [5]. Energy generated from lignocellulosic biomass contributes to about 10% of the global energy requirement [6]. Agricultural and forest residues solely put up the energy of 30 EJ, which is a significant number, to 4500 EJ of the annual utilization of energy [7].

Lignocellulosic materials can potentially be converted into value-added products such as biofuels, primarily bioethanol, bio-oil, gasoline, and chemicals. Different types of conversion technologies are available that follow thermal, thermochemical, and biological routes for lignocellulosic biomass conversion. Thermal conversion is attributed to the burning of biomass for power and heat generation. The transformation of biomass with the application of high temperatures and chemicals is known as thermochemical conversion. It is subdivided into processes such as pyrolysis and gasification. The output of these processes is bio-oil and gasoline along with some chemicals. Bioconversion is essential for converting biomass into biofuels with the aid of microorganisms. Primarily, its main product is bioethanol; however, it also produces bio-butanol, methane, and a few chemicals [8].

Pretreatment is required before bioconversion, thereby separating the components of biomass for efficient fermentation. However, the utilization of feedstock requires a large expenditure of power, heat, and labor during the conversion. The crux of the matter is the expensive pretreatment step that elevates the overall cost of bioconversion. At present, the most effective pretreatments are chemical and physicochemical methods. However, they are not environment-friendly and form toxic substances such as furfural. Therefore, eco-friendly biological pretreatment methods are occasionally employed, although they give lower yields of fermentable sugars [9].

Integrated biorefineries work by combining primary conversion, separation, and downstream upgrading methods to maximize the utilization and value of biomass to generate collective energy [10]. It is a prerequisite for cost-effectively encouraging sustainable energy. However, their application at a commercial scale is a challenge [11]. The recent literature has addressed lignin chemistry and valorization [12,13], cost reduction strategies [14], sustainability factors of pretreatment processes [15], pros and cons of different pretreatment methods [16,17], and conversion pathways of lignocellulosic biomass [18,19].

Currently, there is no review article connecting the conversion of lignocellulosic biomass into sustainable energy systems by using cost-effective strategies. This review fills these gaps by comparing different conversion pathways and pretreatment steps and assessing them based on cost and sustainability, consequently moving towards a greener approach that is integrated biorefineries. It highlights the importance of lignocellulosic biomass and its ability to be converted into bioenergy by different conversion pathways. Moreover, it includes a brief overview of pretreatment methods and their role in sustainable energy production. An attempt is made to discuss the existing and emerging areas to the best of the authors' capability.

2. Lignocellulosic Biomass Structure

Lignocellulose is an integral part of plant cell walls, having a complicated network of polysaccharides, i.e., cellulose and hemicellulose linked to lignin. Its characteristic feature is its recalcitrance due to the high rigidity and robustness of its structure, making it resistant to depolymerization [20]. Cellulose is a crystalline structure that consists of closely packed glucose monomers linked by β -1,4 glycosidic bonds forming tight polymer chains. The high number of hydroxyl groups present at its lateral fibers promotes hydrogen

bonds, making it more stable and, therefore, impervious to depolymerization [21]. It constitutes 30–50% of lignocellulosic biomass. Hemicellulose is a branched polysaccharide that is amorphous and has a lesser degree of polymerization. This attribute makes it more susceptible to degradation than cellulose. Its structure consists of randomly dispersed fiveor six-carbon sugars, with xylan being the main structural unit [20]. Hemicellulose acts as a matrix material in the structure of lignocellulosic biomass as it attaches non-covalently to the cellulose fibers [21]. It comprises 15–35% of lignocellulosic biomass. Lignin is the second most abundant polymer on earth that is hydrophobic [20]. It is a heteropolymer that consists of monomers of coniferyl, coumaryl, and sinapyl alcohols. It acts as a glue that connects cellulose and hemicellulose fibers in lignocellulosic biomass by filling the spaces between them, thereby exhibiting a 3D cross-linked, stable molecular structure. This stability makes it recalcitrant and resistant to degradation [21]. It constitutes 10–20% of lignocellulosic biomass [20]. The potential of feedstock for biorefinery is determined based on the chemical composition of lignocellulosic biomass. Agricultural residues such as wheat straw, sugar cane bagasse, and rice straw have been reported to be commonly used as they have lower lignin content, less than 20 wt%, and higher cellulosic and hemicellulosic content. However, forest residues have a high lignin content, so they are not preferred for biorefinery feedstock. Low lignin content promotes a cost-effective pretreatment and conversion into biofuel [22].

All components of lignocellulosic biomass are capable of producing value-added products. Figure 1 displays these components of lignocellulosic biomass along with their products. Lignin is the principal recalcitrant component in lignocellulosic biomass due to its complex properties such as its chemical composition and molecular weight. It inhibits biological conversion by retarding the activity of enzymes as they bind non-productively. Moreover, high lignin content prevents access of cellulase enzyme to cellulose. It hinders the fermentation process, consequently affecting the efficiency of bioethanol production. Therefore, delignification is a must to improve biological conversion [23]. Lignin can also be directly burned to generate heat and power or can be treated thermochemically to produce low-grade fuels, phenolics, and adhesives. Cellulose and hemicellulose are polysaccharides; therefore, they are potential precursors of fermentable sugars such as glucose and xylose. Bioconversion of these reducing sugars produces bioethanol. Thermochemical conversion of cellulose produce fuels such as bio-oil and gases along with certain chemicals and solvents.



Figure 1. Structure of lignocellulosic biomass and the products of its components [23].

Establishing integrated biorefineries is a pressing need for amplifying the energy output, which is a cost-effective technique that ensures sustainability. An integrated biorefinery works by fusing the total energy obtained from all the components of biomass. All the possible methods are merged to attain the maximum amount of energy [3].

3. Routes of Lignocellulosic Conversion

Lignocellulosic conversion into bioenergy depends upon the processing of biomass by several routes including (i) thermal conversion via combustion, (ii) thermochemical conversion by gasification and pyrolysis, and (iii) biological conversion that involves the use of biocatalyst. Figure 2 sketches the course of lignocellulosic biomasses' conversion into their products [23,24].



Figure 2. Sequential diagram of different lignocellulosic conversion pathways into value-added products.

3.1. Thermal Conversion

Direct burning of lignocellulosic biomass at high temperatures yields thermal energy and ash particles. The thermal energy acquired can be deployed for power and electricity generation. It is a cheap process that is well developed on a commercial scale. However, it is not an environment-friendly method as ash particles pose serious pollution problems [24].

Combustion

Biomass undergoes direct combustion at high temperatures (800–1600 °C) that give rise to thermal energy. When the fuel reacts with oxygen, thermal energy is obtained along with flue gas that consists of CO_2 and water. The temperature of the flame can exceed 1650 °C and depends on the moisture content and heating value of the fuel, construction of the furnace, and the fuel-to-air ratio [24]. European countries commonly practice combustion at a commercial scale by using biomass pellets due to their higher efficiency [25]. Biomass that has a moisture content of less than 50% is preferred for this process [26]. Combustion

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is conducted at various scales by using diverse equipment such as boilers, stoves, turbogenerators, and turbines. It is essential in converting chemical energy in the biomass into mechanical power and electricity [27]. Burning fuels provoke soaring emissions of carbon dioxide, particulate matter, NO_x , and ash. These emissions pose serious pollution threats [28].

3.2. Thermochemical Conversion

A physical catalyst or heat is employed to convert biomass into liquid or gas that is further upgraded into biofuel. This method requires high power and energy consumption. The chemicals used are often expensive, which produce inhibitors as a byproduct. Clean-up processes for emissions and wastes necessarily add to the overall cost of the process [24].

3.2.1. Gasification

Gasification is a thermochemical process that entails the reaction of biomass with oxygen, air, or steam to produce a mixture of gases, i.e., CO_2 , CO, CH_4 , H_2 , N_2 , and hydrocarbons known as producer gas, syngas, or synthetic gas varying in proportions of the component gases [29]. The main objective of gasification is to produce a maximal yield of gaseous products and minimize the yield of unreacted char and condensable hydrocarbons [8]. Currently, three notable types of gasification processes exist in the form of the fluidized bed, fixed bed, and entertained flow. The fluidized bed is subdivided into a bubbling, dual, and circulating fluidized bed. Fixed bed stems into updraft, downdraft, and crossflow. They differ by the mode of feeding biomass into the gasifier, from the side or top, with the gas flow or under gravity, and the greater or lower melting point of biochar and ash [30]. Table 1 categorizes various industrial plants of gasification based on their gasifiers. The main steps of gasification include the generation of syngas followed by its clean-up process and Fischer–Tropsch synthesis [31].

Table 1. Classification of gasification plants at industrial scale.

Gasification Type	Temperature Range/°C	Location of Industrial Plant	Type of Biomass	End Product	Functional Unit	References
Fixed bed			700-800			[32]
		Liaoning, China	Wood residues	Gas for cooking	700 kWt	
Downdraft		Jilin, China	Agricultural residues	Power and heat	200 kWe	[33]
		Hunan, China	Crop residues	Gas for cooking	300 kWt	
		Vilhelmina, Sweden	Wood chip	Heat	4–6 MWth	
Updraft		Harboøre, Denmark	Wood chip	Heat and power	4 MWth	[34]
		Ankara, Turkey	Wood chip	Heat and power	2 MWe	-
Fluidized bed			1000 °C			[32]
		Värnamo, Sweden	Wood chips	Heat and power	6 MWe/9 MWth	[35]
		Ruien, Belgium	Woodchip	Syngas used to power Pulverised Coal (PC) boilers	50 MWth	
Circulating fluidized bed	-	Varkaus, Finland	wood	Biomass to liquid fuel (diesel), Syngas used for lime kiln	50 Mwth	[34]
		Lahti, Finland	Forest residues, sawdust, short rotation forest (SRF), and bark	Syngas used to power PC boilers	45 MWth	-
		Vaskiluodon Voima Oy, Finland	Forest residue	Co-firing	140 MWth	-

Gasification Type	Temperature Range/°C	Location of Industrial Plant	Type of Biomass	End Product	Functional Unit	References	
Bubbling		Jiangsu, China	Rice husk	Heat	120 MWth	[22]	
fluidized bed		Anhui, China	Rice husk	Electricity	400 kWe	[33]	
		Oberwart, Austria	Wood chip	Heat and power	10 MWth	[24]	
Dual fluidized bed	ea	Güssing, Austria	Wood chip	Heat and power	8 MWth	[34]	
Entrained		1400–1500 °C				[32]	
		Freiberg, Germany	Wood	Biomass to liquid fuel	45 MWth	[34]	

Table 1. Cont.

Syngas is generated in a gasifier by applying a temperature of 600–1000 °C to the gasifier, either directly or indirectly. A residence time of 3–4 s is given for a productive gasification reaction. The initial product of this reaction is a raw gas that is cooled in a heat exchanger and fed into a cyclone to separate solid particles from the exhaust gas. Impurities in the natural gas are removed by scrubbing of water or solid adsorption in the packed bed. Subsequently, a water–gas shift reaction is accomplished to adjust the H₂/CO ratio of the raw gas to produce syngas consequentially. This syngas is passed over metal catalysts such as Ni, Cu, Fe, Co, Rh, and Ru in Fischer–Tropsch (FT) synthesis, yielding hydrocarbons [36]. This process can crop up at both high and low temperatures. At high temperatures of 320–375 °C, short-chain molecules are obtained by using iron as a catalyst in a two-phase fluidized bed reactor. At low temperatures (200–250 °C), long-chain molecules are acquired by using cobalt or iron as a catalyst in a tubular fixed bed reactor or a three-phase slurry reactor [37].

Gasification produces heat that can be utilized by boilers or kilns. Undesirable compounds such as tars are consumed due to the burning of gas; therefore, the syngas used is minimally cleaned. Syngas can be used in internal combustion engines if tar is not overloaded and the chief part of the particulate matter is removed from the gasifier. Gas turbines further promote integrated gasification-combined cycle power with high efficiency, although effective gas cleaning is required. Syngas is crucial for the synthesis of various fuels and chemicals including alcohol, organic acids, hydrocarbon fuels, and esters. The catalysts in these syntheses are more sensitive to contamination as compared to the gas turbines [24].

Gasification has a wide range of applications as it is essential for hydrogen production, thermal power generation, and the synthesis of chemicals and fuels. This encourages gasification-based energy refineries that produce a mix of chemical products and energy. Introducing these biorefinery technologies commercially would mark the beginning of a new era [38].

3.2.2. Pyrolysis

Pyrolysis is a thermochemical conversion that takes place as either an initial step to combustion and gasification or can be carried out itself for biofuel production. Pyrolysis is the decomposition of lignocellulosic biomass into a volatile and carbon-rich solid at a temperature ranging from 300 to 900 °C in the absence of oxygen [36]. The products of this process are bio-oil (liquid form), biochar (solid state), and fuel gas (gaseous state) [32]. It can be further classified into slow, fast, intermediate, and flash pyrolysis depending upon the operational conditions. In slow pyrolysis, low temperature and heating rate are required with a longer residence time. Solid char is the main product of this reaction. In fast pyrolysis, high temperature and heating rate are needed with a short residence time, as these conditions aid in minimizing char formation. In intermediate pyrolysis, a moderate climate and heating rate are required. Flash pyrolysis, in contrary to the other pyrolysis types, has the highest temperature and heating rate with the shortest residence time and requires special reactors for achieving such condition [26].

Fast pyrolysis produces aerosols and condensable vapors that result in the formation of an energy-rich liquid, bio-oil. It is the chief product of fast pyrolysis with a yield of 70–80 wt%. Bio-oil is a liquid that is dark brown or black in color which is a complex mixture of 30 wt% water and oxygenated organic compounds such as acids, ketones, aldehydes, phenolics, esters, alcohols, ethers, furan, oligomers of high molecular weight, and nitrogenous compounds [39]. Other products formed include biochar, syngas (flammable gas), and anhydrous sugars that are obtained in significant quantities under suitable processing conditions. The biochar formed is majorly composed of carbon, which is separated from other products by a cyclone, and the solid product developed can be used as a fuel. Non-condensable gases are collected during vapor condensation, as these can be recycled. They are used as fuel or reused as a fluidizing gas in the pyrolysis reactor. The thermolytic sugars can also be catalytically upgraded into fuel or can be fermented [24].

Fast pyrolysis produces liquid fuel directly, which is readily stored and transported to remote areas where energy is required. It makes it an alternative to petroleum-based fuels. However, initially, the use of bio-oil as fuel for turbines of gas engines and boilers was costly, corrosive, and unstable during its storage. According to current strategies, bio-oil can be upgraded into substitutes for heavy fuel or transportation fuels. Hydrotreatment of bio-oil into hydrocarbons is conducted to boost it by contracting its oxygen content and hydrophilicity. This upgrading is technically feasible; however, it is an expensive process [40].

3.3. Biological Conversion

Bioconversion converts biomass into biofuel by using biocatalysts either directly or in a prior pretreatment step. Complex sugars are converted into intermediate sugars which are fermented to produce biofuels such as ethanol [41]. Enzymes or a consortium of microorganisms act as biocatalysts that facilitate this conversion. It is a highly selective process that has high conversion efficiency. However, it is a time-consuming method with an incredibly high cost of pretreatment, denoting the infeasibility of the process [42].

3.3.1. Direct Conversion

Direct microbial conversion (DMC) or consolidated bioprocessing (CBP) is an approach in which enzymatic hydrolysis is integrated with fermentation to produce valueadded products by utilizing a consortium or a single organism. Lignocellulosic biomass is directly converted into biofuels without pretreatment. Microorganisms are genetically engineered such that they can hydrolyze the biomass as well as can carry out fermentation. Many thermophilic anaerobic microorganisms possess cellulolytic properties that are employed to carry out this conversion. For example, *Clostridium thermocellum, Caldicellulosiruptor* sp., *Monilia* sp., *Paecilomyces* sp., and *Neurospora crassa* [43].

Valdez-Vazquez et al. [44] conducted two-stage consolidated bioprocessing of wheat straw. In the first stage, 79.5 mL H_2/g of hydrogen was produced by utilizing a microbial consortium made by integrating species of epiphytic *Enterococcus*. Acetone–butanol–ethanol (ABE) was produced in the second stage by employing a co-culture of *Clostridium cellulovorans* 35296 and *Clostridium beijerinckii* 10132. Then, 23.3 g/L of ABE was produced within 5 days. Untreated wheat straw components were degraded to make cellulose available to produce ABE. Chen et al. [45] experimented with consolidated bioprocessing of untreated rice straw by using anaerobic sludge to produce a hydrogen yield of 2408 mL H_2/g TS.

This conversion is economically viable since the production cost of separate commercial enzymes for hydrolysis is reduced. It requires less time as an extra step of hydrolysis is skipped. Likewise, accumulated sugars no longer inhibit the activity of cellulases as they are immediately consumed for fermentation [46].

3.3.2. Indirect Conversion

Lignocellulosic biomass is initially hydrolyzed into fermentable sugars, and subsequently, these sugars are fermented into biofuels. Two types of fermentation can be carried out after the pretreatment: either separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF). In separate hydrolysis and fermentation (SHF), saccharification and fermentation are performed sequentially. This is denoted as the indirect conversion of pretreated lignocellulosic biomass. However, in simultaneous saccharification and fermentation (SSF), both processes occur in a single fermenter. This is the direct conversion of pretreated lignocellulosic biomass into biofuels [47].

Pretreatment Technologies

Pretreatment is the conversion of lignocellulosic biomass into fermentable sugars and it requires high consumption of energy and costly chemicals [48]. It is the most expensive step as it constitutes at least 20% of the production cost of the entire conversion by using different approaches [49]. The main objectives for effective pretreatment are to (1) obtain maximum sugar yields, (2) treat a wide range of lignocellulosic feedstocks, (3) ensure lignin recovery to carry out combustion, and, subsequently, (4) produce a few inhibitors or co-products and (5) minimal operational costs and energy consumption [50]. Figure 3 shows a schematic representation of the effect of pretreatment technologies on lignocellulosic biomass.



Hemicellulose

Figure 3. Degradation of lignocellulosic biomass into cellulose, hemicellulose, and lignin via pretreatment [23].

For choosing an appropriate pretreatment method, a few factors must be considered, including the type of lignocellulosic feedstock to be treated, the economic feasibility of the process, and its impacts on the environment [50]. Figure 4 displays several types of pretreatment methods. These methods are described below concerning the recent findings by highlighting their pros and cons.



Figure 4. Flowchart of different pretreatment technologies.

Physical Methods

Mechanical Extrusion

This is the most typical pretreatment in which lignocellulosic biomass is disintegrated into smaller cross-sections. The crystalline and amorphous cellulose matrix within the biomass is disrupted. This disruption is aided by the combination of high temperatures in the barrel and shear force that is produced by the rotating screw blades in the extruder [48]. There are several types of extruders; however, twin-screw and single-screw extruders are widely used for the pretreatment of lignocellulosic biomass, which further enhances the enzymatic hydrolysis [51]. Since this method requires a large amount of energy consumption, it is costly and scaling up for industrial processes is quite difficult. The advantages of this method are that it is a controlled process with enhanced monitoring, it is highly flexible to any alterations in the process, products formed are with minimum degradation of sugar, and it can recover sugar from different types of biomass [52].

Sugar recovery can be further enhanced by combining extrusion with other methods—for example, chemical treatment with acid or alkali, ammonia fiber explosion, steam explosion, bio-extrusion, and vacuum extrusion. These methods in combination also reduce the cost of pretreatment to an extent. Table 2 gives a brief description of different types of extrusion methods in combination with other methods for pretreatment [53].

Types of Extrusion Methods Used in Combination	Description of the Process	References
Steam explosion extrusion	High pressure and high steam temperature are applied to treat the biomass for a short time and then this pressure is released by extrusion. This results in the expansion of steam that provides a shear force for the disruption of the cell wall of the plant cell.	[54]
Acid extrusion	Pretreatment of biomass is done by dilute acid and then this is added to the hot water extraction system.	[55]
Alkaline extrusion	Biomass is soaked in NaOH solution and added to the extruder with the help of a volumetric pump. The alkali acts as a delignification agent and prevents carbohydrate degradation.	[56]
Vacuum extrusion	Biomass is treated in vacuum extrusion.	[57]
Ammonia fiber explosion and extrusion	Biomass is extruded with ammonia that aids in expanding the fiber.	[58]
Extrusion and heat moisture treatment	Heat moisture treatment and extrusion are used in combination to pretreat the biomass with physicochemical properties.	[59]

Table 2. Summary of different types of extrusion methods used in combination.

Milling

This process reduces the size of biomass and increases its surface area by milling, chipping, and/or grinding. Shear forces have been generated that aid in breaking down the crystalline structure of cellulose in the biomass. Chipping reduces the size of biomass to 10–30 mm, whereas milling and grinding further reduce the size of the particles to 0.2 mm [60]. However, it was found by Mosier et al. [61] that size reduction below 0.4 mm does not significantly affect the yield and rate of hydrolysis. Some parameters are considered for carrying out effective milling such as initial biomass size, feeding rate of biomass, time, machinery parameters, and moisture content of biomass [62,63].

The type of milling and its duration time depend upon the kind of biomass that is used. Milling methods that are commonly applied include hammer milling, two-roll milling, vibratory milling, and colloid milling [60]. More recent and effective milling techniques that reduce the size of biomass vary greatly from the common standard milling method, including vibratory ball milling, which improves the digestibility of chips of aspen and spruce. Wet disk milling is a widespread technique due to its low energy consumption. Disk milling produces fibers and helps in enhancing the hydrolysis of cellulose. Milling is advantageous over other physical methods of pretreatment as it has a short processing time, less energy is consumed in this method, and water consumption is also reduced [20].

Sonication

In this technique, ultrasonic waves are applied through a fluid containing lignocellulosic biomass. These acoustic waves produce microcavities within the biomass, causing variation in pressure. Due to this pressure difference, shock waves are generated which produce gas bubbles that collapse within the microcavities subsequently. Shock waves give rise to mechanical disruption of the biomass. The frequency of ultrasound that is used is 10–100 kHz, which causes the degradation of polymers within the biomass and promotes maximum cavitation. According to a study by Yachmenev et al. [64], when ultrasonic waves are exposed to a cellulosic suspension at 50 °C, the rate of enzymatic hydrolysis is roughly increased by 200%. Pretreatment with sonication is dependent on several factors such as biomass characteristics, ultrasonic frequency, duration of ultrasonic frequency, reactor configuration, reactor geometry, kinetics, and the solvent used in the pretreatment [1,65]. However, although this technique is costly, it can pretreat biomass at low temperatures within a short period [66].

Pulsed Electric Field (PEF)

This method helps in exposing cellulose within the biomass by producing pores in the cell membrane of the plant cells. This method further facilitates the entry of agents that reduce cellulose into fermentable sugars [67]. A burst of high voltage for short durations (i.e., nanoseconds to milliseconds) is given, ranging from 5 to 20 kV/cm. The pros of this method are that ambient conditions are required for this treatment since short durations of pulse time are provided, so the energy needed for this method is lower [48].

Chemical Methods

Alkaline Pretreatment

This is a simple method with a strong effect, so it is considered a reliable method. Alkalis are used to break the alkyl-aryl linkages present in lignin within the lignocellulosic biomass. Alkaline solutions such as sodium hydroxide, calcium hydroxide, sulfite, ammonium hydroxide, and lime are used for this purpose [68]. Sodium hydroxide is the most used alkaline solution as it is an effective delignifying agent and is capable of working in different conditions. In this method, delignification is carried out selectively by increasing the surface area and porosity of biomass as well as preventing the loss of carbohydrates and reducing sugar. It also improves the digestibility of enzymes used in hydrolysis, making it essential for enzymatic hydrolysis, as a maximum yield of fermentable sugars can be obtained [69]. Alkalis are less aggressive reagents as compared to acidic solutions, for example, sulfuric acid, used in acidic pretreatment. However, the biggest drawback of this method is its long reaction time as it requires many hours to 1 day for its operation [9,66].

Acid Pretreatment

The use of acids for pretreatment has been reported by various studies on bioethanol production [70,71]. Acidic pretreatment works on lignocellulosic biomass by increasing hemicellulose degradation. The structure of lignocellulosic biomass is changed as hemicelluloses are converted into soluble sugar. This conversion can be further enhanced by the increase in temperature. The acid works by breaking the linkages between polysaccharides and lignin, thereby recovering the maximum amount of monomeric sugars [72]. Commonly used acids include sulfuric acid, phosphoric acid, and acetic acid. To make the method effective, a few parameters are considered important such as the concentration of acid, solid loading, residence time, and temperature. This method is preferred over other methods as it ensures disruption of the lignocellulosic matrix and conversion of amorphous cellulose. However, it promotes inhibitor formation, which means more energy consumption and a high cost of acid recovery [71]. A common example of acid pretreatment is dilute acid pretreatment, which employs diluted acid rather than concentrated acid for hydrolysis. This method consumes a lower amount of acids at higher temperatures to obtain a reasonable yield of glucose from cellulose [73].

Ionic Liquid Pretreatment

Lignocellulosic biomass is highly soluble in ionic liquids (ILs). Anions and cations in ionic liquids facilitate the depolymerization of lignin and cellulose in the biomass [74]. However, using ionic liquids imparts negative effects on cellulase activity and efforts are underway to increase the resistance of the enzymes [75]. The rate of hydrolysis during ionic liquid pretreatment is affected by biomass loading and temperature. Various types of ionic liquids used include pyridinium-based $[(C_5N)X_n]^+$, imidazolium-based $[(C_3N_2)X_n]^+$, pyrrolidinium-based $[(C_4N)X_n]^+$, phosphonium-based $[PX_4]^+$, ammonium-based $[NX_4]^+$, and sulfonium-based $[SX_3]^+$ ILs. Acidic ionic liquids are a type of ionic liquids that have a high potential for lignocellulosic biomass pretreatment. They play a primary role in lignin depolymerization as they break the ether linkage, thereby extracting lignin [76]. Although costs of chemicals can be reduced by using solvents such as ionic liquids with high water content for the pretreatment of lignocellulosic biomass [77], this method has certain disadvantages such as the fact that the recycling of pure ionic liquids requires a large amount of energy, making it a costly method, and more waste is generated, making it difficult to recover.

Organic Solvent Pretreatment

Organic solvents can fractionate lignocellulosic biomass into pure forms of lignin, cellulose, and hemicellulose, making the recovery and reuse of solvents easy. These solvents are used with or without a catalyst for lignocellulosic biomass pretreatment. According to the literature, the conversion from biomass to sugars is enhanced using organic solvents [78]. Widely used organic solvents include alcohol, esters, phenol, acetone, propionic acid, dioxane, amines, and formaldehyde. Alcohols with low boiling points such as methanol and ethanol are preferred as they have a low cost and can be recovered easily.

A common type of organic solvent pretreatment is Organosolv. This method employs the use of aqueous organic or organic solvents within the temperature range of 100–250 °C. This method is advantageous as a highly pure form of cellulose is separated with minimum degradation and the high efficiency of hemicellulose is fractionated. However, the production of pure lignin and chemicals of its derivatives along with high-value co-products poses serious economic concerns [79].

Ozonolysis/Plasma

The lignin content in lignocellulosic biomass is primarily reduced by using ozone (O₃) treatment, and this method does not affect cellulose and hemicellulose. The moisture content of biomass is a significant factor that affects the pretreatment by ozone, as oxidation of lignin reduces with an increase in moisture content. This method is advantageous over other chemical methods as it is conducted at ambient temperature and pressure. It is an environmentally friendly method as no toxic inhibitors are produced and this cannot further affect hydrolysis and fermentation. Despite the effectiveness of the method, it is expensive, as a large amount of ozone is required, making it infeasible to conduct at an industrial scale [66]. Recently, research by Kumari and Singh [80] is being carried out in different areas to make this pretreatment method economical, such as by generating feasible ozone concentrations at an industrial scale.

Physio-Chemical Methods

Steam Explosion

In a steam explosion, biomass is pretreated by heating it in a reactor that contains saturated steam at significantly high pressures ranging from 0.69 to 4.83 MPa and within a temperature range of 160–260 °C. The residence time of the biomass in the reactor might vary from seconds to minutes [66]. The process works as the vapors condense and penetrate the biomass, provoking autohydrolysis. This results in the formation of organic acids from acetyl groups that are present within the biomass. These organic acids are responsible for the breakage of hemicellulose and glycosidic bonds that are present in the biomass. The lignocellulosic matrix is disrupted as the hemicellulose is solubilized [81]. The drawbacks of this method are that it produces fermentation inhibitors and requires high water and energy consumption, thereby increasing the overall cost of the process [66].

Hot Water Pretreatment

Hot water pretreatment is also referred to as hydrothermal pretreatment. In this method, lignocellulosic biomass is pretreated with liquid water having a temperature within the range of 140–240 °C. As a result, hemicellulose is depolymerized and the products formed are dissolved in the liquid phase, whereas the cellulose is not disturbed and is still present in the solid phase. Lignin undergoes depolymerization and polymerization simultaneously due to the temperature of the water. Since the temperature of glass transition of lignin in aqueous conditions is between 80 and 100 °C [66], relocalization of lignin occurs, improving the digestibility of cellulose as this migration promotes access to cellulose microfibrils [82]. This technique is considered a green technology as chemical reagents

are not required, which also reduces the cost of the process [83]. However, increasing the severity of the process produces enzyme inhibitors [84].

Supercritical CO₂ Explosion

Supercritical CO₂ is a non-flammable solvent that does not emit organic vapors and is considered a green solvent. Its critical pressure (P_C) and temperature (T_C) are 1071 psi and 31 °C, respectively. The solvent can be separated easily after pretreatment. CO₂ is released explosively through a nozzle at high pressure that breaks down the structures of cellulose and hemicellulose in the biomass, thereby increasing their surface area for hydrolysis subsequently [85]. To maximize the yield of specific compounds, several factors can be changed or modified such as pressure, temperature, size of temperature bed, and flow of solvent. It is an economical method that produces no toxic products and reduces greenhouse emissions with the utilization of CO₂. This method can be used in combination with extrusion and sonication to make the pretreatment more effective [86].

Ammonia Fiber Expansion (AFEX)

The pretreatment of lignocellulosic biomass is performed by expansion with ammonia fiber. The biomass is applied with gaseous or anhydrous ammonia that is pressurized in a container. Briefly, 1–2 kg of liquid ammonia is applied on 1 kg of dried biomass at a temperature of 90 °C and a residence time of 30 min [66]. When highly pressurized ammonia is added at a high temperature, it decrystallizes cellulose, deacetylates the acetyl groups, and depolymerizes the hemicellulose present in the biomass. This method is advantageous as the gas recycling system that is connected to the main system can reuse ammonia several times [87]. Therefore, the overall cost of this pretreatment is low as the cost of ammonia and its recovery is saved by reusing it. Inhibitors are also not produced, further easing the downstream processing [88].

Microwave Pretreatment

Lignocellulosic biomass is pretreated by irradiating microwaves on it. These waves accelerate the biological, physical, and chemical processes within the biomass. As the polar molecules within the biomass start vibrating, the movement of the ions also starts generating heat and collisions. The performance of this method greatly depends on the properties that the lignocellulosic biomass exhibits, such as dielectric properties. This method does not produce toxic products; however, using microwaves is expensive [67].

Wet Oxidation

Hydrogen peroxide or water is used to treat biomass in the presence of oxygen/air at a high temperature that is greater than 120 °C for 30 min. This method is essential for biomass that is lignin-enriched. The effectiveness of the process depends upon temperature, the pressure of oxygen, and the reaction time. Water behaves like an acid that catalyzes hydrolytic reactions in this process when the temperature is raised above 170 °C [48]. The lignin present in the biomass oxidizes, while hemicellulose breaks into its monomers of pentose sugars. Cellulose is least affected by this method as it is not completely broken down. Chemical agents such as alkaline peroxide and sodium carbonate are added, which reduces the temperature of the reaction and further improves the degradation of hemicellulose and decreases the formation of inhibitors such as furfurals and their aldehydes. This pretreatment is infeasible at an industrial scale as hydrogen peroxide is costly and storage of pure oxygen is a hindrance due to its combustible nature [89].

Biological Methods

Biological pretreatment of lignocellulosic biomass is achieved with the aid of microorganisms. Several microbes can synthesize cellulolytic and ligninolytic enzymes. They work by degrading components of lignocellulosic biomass by delignification, consequently allowing the excess to polysaccharides for hydrolysis [48]. Fungal species are used frequently

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as they possess a wide range of enzymes for efficient degradation. White rot fungi remove lignin by their enzymatic complexes; in contrast, brown rot fungi could degrade hemicellulose and cellulose. The enzymes used to perform this action include endoglucanases and β -glucosidases. Soft rot fungi degrade cellulose as they possess enzymes such as exo-1,4- β -glucanase, endo-1,4- β -glucanase, and 1,4- β -glucosidase. They also grade lignin partially due to the presence of laccase enzymes [90].

However, a single species of microbe cannot carry out activities productively. Therefore, utilizing more than one species collectively as microbial consortia acts as a helping hand for effective pretreatment. Microbial consortia are referred to as the communities formed by highly diverse microorganisms that undergo interactions in different ways, either with cooperation or with competition [91]. Commonly used microorganisms for forming a consortium include bacteria such as *Cytophaga* and *Cellulomonas* and several fungi such as *Penicillium, Aspergillus, Humicola*, and *Tricoderma* [92]. This method is considered environment-friendly as low energy is required and chemical reagents are not used. However, it is not industrially viable as long incubation times make it uneconomical [66]. Table 3 gives a brief overview of the limitations of the pretreatment technologies and their consequences by shedding light on the recent literature.

Pretreatment	Limita	tions	Sorted Examples	References	
	Inhibitor production	Process Cost *	Feedstock Results		
			Physic	al Methods	
Mechanicalextrusion	Low	High	• Vine trimming shoots	• 40% increase in methanol production.	[93,94]
Milling	Low	Low	Corn stoverRice straw	 Ball milling enhanced the yield of ethyl levulinate by 31.23%. Enhanced the yield of ethanol from two digested residues. The ethanol concentration of 10% digested residue and 2.5% digested residue was 147.42 and 116.65 mg/g, respectively. 	[63,91,95,96]
Sonication	Low	High	Grape pomaceAgave durangensis	 Increased methanol production. Reduced the yield of lignin and hemicellulose by 6.3% and 13.3%, respectively. Enhanced the specific activity of the enzyme by 1.5 to 2 times 	[94,97,98]
Pulsed electric field (PEF)	Low	Low	• Wood chip and switchgrass	• Increased the porosity of biomass, thereby amplifying the rate of enzymatic hydrolysis.	[99]
			Chemi	cal Methods	
Alkaline pretreatment	Low	High	 Rice straw Bagasse Commercial Bamboo chips 	 Treatment with sodium carbonate enhanced the concentration of glucose and, subsequently, ethanol. The concentration of total sugars and ethanol obtained was 137.3 and 83.1 g/L, respectively. Treatment with sodium hydroxide gave a maximum yield of bioethanol of 7.05 g/L. Treatment with sodium hydroxide increased the amount of total sugars by 70% to 85%. 	[94,100–102]

 Table 3. Summary of limitations and recent literature of different pretreatment technologies.

Pretreatment	Limita	tions	Sorted Examples	References	
	Inhibitor production	Process Cost *	Feedstock	Results	
Acidic pretreatment	High	High	Corn stover and cornWheat straw	 Treatment with sulfuric acid gave a bioethanol yield of 99.3 g/L. Treatment with 2% of sulfuric acid gave a bioethanol yield of 0.44 g/L. 	[78,103,104]
Ionic liquid	Low	High	Sugarcane bagasse	• Treatment with poly ethylene glycol (PEG) gives a high rate of enzymatic hydrolysis and yield of bioethanol of about 84%.	[94,105]
Organic solvent	High	High	• Wheat straw	• Treatment with 60% ethanol extracted lignin with a yield of more than 90%.	[63,106]
Ozonolysis	Low	High	Maize stover	• 78% of lignin was removed and the yield of glucose was increased from 18.5% to 80% after enzymatic conversion.	[107]
			Physioche	emical Methods	
Steam explosion	High	High	 Switchgrass Empty fruit bunches (EFB) of palm oil 	 A maximum saccharification yield of 83% was attained. Optimum results were obtained at 195 °C within a time of 6 min. An increase of 34.69% in glycan content with a decrease of 68.125% in hemicellulose content in the pretreated biomass was observed. 	[94,108,109]
Hot water pretreatment	Low	Low	Bamboo samples	• The maximum reducing sugars yield obtained was 42.21% at 180 °C for 25 min.	[94,110]

Table 3. Cont.

Pretreatment	Limitations		Sorted Examples of Recent Studies of Pretreatment Technologies		References
	Inhibitor production	Process Cost *	Feedstock	Results	
Supercritical CO ₂ explosion	Low	High	• Corncob, corn stover, and sorghum stalk	• This experiment resulted in a 3–4-fold increase in the yield of sugars obtained from enzymatic hydrolysis of lignocellulosic biomass in comparison to the biomass that was not pretreated with supercritical CO ₂ pretreatment.	[63,111]
Ammonia fiber expansion (AFEX)	Low	Low	Agave bagasse	• All the carbohydrates in the samples of biomass were preserved and the sugar yield of xylose and glucose obtained from hydrolysis was 42.5%.	[63,112]
Microwave pretreatment	Low	High	Sugarcane bagasse	• Reducing sugar yields obtained were 4 times greater with pretreatment assisted with microwave method and time duration was 5.7 times less.	[94,113]
Wet oxidation	Low	High	Rice straw	• An enhanced cellulose recovery of 83.01% and lignin 77.29% was obtained.	[114]
Biological methods	Low	Low	 Corn stover a rice straw Wet sauce and wet rice straw 	 Treatment with a white rot fungus, <i>Irpex lacteus</i>, gave a bioethanol yield of 13.5 g/L from corn stover and 12.5 g/L from rice straw. A fungal consortium of <i>Armillaria gemina</i> and <i>Pholiota adipose</i> was used. Enzymatic hydrolysis of the pretreated biomass obtained a yield of 63.6% and 74.2% for sauce and rice straw, respectively. The hydrolysate converted into bioethanol subsequently further confirmed a good yield of 72.4% 	[115,116]

Table 3. Cont.

* High process cost = >20% of the production cost of lignocellulosic conversion. Low process cost = up to 20% of the production cost of lignocellulosic conversion [49].

Enzyme Digestibility

Enzymatic digestion is achieved by using cellulases and hemicelluloses that transform cellulose and hemicellulose into usable energy sources. The three potent cellulase enzymes that carry out this step are endo- β -1,4-glucanases (EC3.2.1.4), exo- β -1,4-glucanases such as cellobiohydrolase (CBH) (EC3.2.1.91), and β -glucosidase (EC3.2.1.21) [117]. Initially, endoglucanases cleave the interior cellulose fibers, forming free ends on which the exoglucanases act to produce cellobiose units. β -glucosidase further hydrolyzes these units into glucose. Feedback inhibition of cellulases is a major challenge as glucose, the final product of hydrolysis, inhibits β -glucosidase, thereby affecting hydrolysis [118]. Hemicellulose is hydrolyzed by using enzymes such as xylanases, β -xylosidase, glucomannanase, galactomannanase, and glucuronidase [66].

Recently, copper-dependent enzymes, lytic polysaccharide monooxygenases (LPMOs), have changed the view of employing hydrolytic enzymes only for the degradation of cellulose and hemicellulose. LPMOs can increase the efficiency and reduce the cost of fermentation [119]. They improve biomass degradation by an oxidative mechanism. Oxygen is reduced by copper ions in the presence of an electron donor (ascorbic acid and cellobiose dehydrogenase (CDH)). Subsequently, the reduced oxygen takes hydrogen ions from the substrate, resulting in the cleavage of the β -1,4 glycosidic bond. LPMOs make an entry point for cellulases to act by oxidizing the glycosidic bond. The N- and C-terminal of the active site of LPMOs consists of histidine complexed with copper [120]. AA9 LPMOs increase the yield of glucose and reduce the number of cellulase enzymes in saccharification [121]. According to a report [122], the (TRAA9A) LPMO enhanced the yield of hydrolysis as it separated the cellulose ribbons, which increased the accessible surface area of bacterial microcrystalline cellulose.

The advent of recombinant enzymes has also managed to garner attention across the world as they are vital in making the hydrolysis step industrially viable by enhancing the sugar yield [123]. For example, thermophilic enzymes are manufactured that can withstand harsh conditions such as high pH and temperature. Moreover, the turnover of sugar content is also amplified. Medina et al. [124] created thermostable recombinant laccases by cloning the WSUCF1 strain from *Geobacillus* sp. into *E. coli*. These enzymes work in concert with other enzymes to hydrolyze bagasse and corn stover; however, laccases do not work in every situation [125]. The results exhibited improved hydrolysis by 1.32–2.02 times and 1.31–3.28 times. Likewise, [126] designed an enzyme *Mt*EG5A expressing the endoglucanase (EG) gene of a thermophilic fungi, *Myceliophthora thermophile*, into a methylotrophic yeast, *Pichia pastoris*. It was observed that these enzymes hydrolyze spruce biomass, birch, and wheat straw to produce an excessive amount of cellobiose and, therefore, high levels of sugars.

Reducing sugars obtained by hydrolysis undergo fermentation to produce biofuels such as bioethanol, acetone, lipids, butanol, *iso*butanol, etc. Solid-state or submerged fermentation is carried out in batch, fed-batch, or continuous systems. Principally, yeast species and fungi are employed to perform fermentation. *Saccharomyces cerevisiae*, a model organism in industrial biotechnology, produces higher yields of ethanol even in limiting conditions of oxygenation [127]. Some fungal species could ferment cellulose into bioethanol such as *Neurospora*, *Paecilomyces*, *Phanerochaete*, *Monilia*, *Sclerotium*, *Aspergillus*, *Penicillium*, *Fusarium*, *Trichoderma*, and *Schizophyllum*. Bacteria that have the potential to produce ethanol industrially include *Escherichia coli*, *Erwinia chrysanthemi*, *Zymobacter palmae*, *Zymonoas mobilis*, and *Klebsiella oxytoca* [8].

4. Integrated Biorefineries for Lignocellulosic Biomass

Biorefineries make use of biomass for processing complexes to produce a wide range of fuels, chemicals, and bio-based materials [128]. Second-generation biorefineries have potential for the production of sustainable energy and chemicals. They utilize feedstocks such as lignocellulosic, non-edible crops and wastes such as black liquor, sawdust, bark, and straw. In contrast to first-generation biorefineries, this approach employs advanced processes, leading to more value-added products. However, several techno-economic constraints such as the high cost of processes and other operational concerns in second-generation biorefineries need to be addressed to make it successful [11].

Integrating different biorefineries exploits the feedstock by producing a maximum amount of value-added products and a minimum amount of waste by converting it into low-value-added products. This amplifies the output and reduces the overall cost [128]. For example, the decreasing demand for paper has led to the current trend of converting pulp mills into integrated biorefineries in the wood industry. Lignin is recovered from black liquor that is used by a pulp mill for wood or paper processing [129]. In 2012, the European Union (EU) introduced a bio-economy strategy with its main motive of developing sustainable biorefineries based on cost-effective lignocellulosic conversion into bioproducts and bioenergy [130]. The EU aims to provide 25% of energy for transportation through biofuels that are derived from biorefineries by 2030 [131]. Many European and other scientists are working to devise ways to cut down the cost of processes [132–138].

Valorization of lignocellulosic biomass can be accomplished by converting the biomass into useful products via three approaches [11]: First, biomass can be fractionated into its components, with subsequent processing of components into products and energy. Initially, recalcitrant lignin is removed via pretreatment to make carbohydrates (cellulose and hemicellulose) accessible for hydrolysis and fermentation to produce bioethanol. The hydrolysate or effluents of fermentation can also be employed for biogas or biohydrogen production by anaerobic digestion and photo/dark fermentation [139]. Recently, a sustainable approach of reductive valorization of lignocellulosic biomass by reductive catalytic fractionation (RCF) has overshadowed other methods. It is also known as the first lignin biorefinery that has succeeded in capturing interest over the last few years. Initially, lignin is extracted from the biomass by using solvents in a process called solvolysis, followed by depolymerization and stabilization using redox catalysts. Phenolic units and monolignol are obtained as a result of this fractionation, which are further used as feedstock for valueadded products such as aromatic chemicals, polymers, bio-based fuels, and drugs [140]. Second, biomass can be partially degraded followed by separation and upgrading into products. For example, bio-oil is produced by pyrolysis that is further upgraded by improving the fuel properties [11]. Third, biomass is completely destructed into syngas by gasification. Syngas is the precursor for hydrogen production in chemical industries or can be converted into fuels and organic chemicals via Fischer–Tropsch synthesis [141]. However, the presence of methane and tar in syngas complexes makes biomass gasification economically unviable. Recently, catalytic biomass gasification has gained attention across the world, which improves the efficiency of gasification by $\sim 10\%$ [142]. The gas produced can also be combusted directly to produce energy. Combustion of biomass and coal collectively is an established technology that is employed to generate combined power and heat and many plants are functional worldwide [143].

Integrating biorefineries is crucial for the cost-effective and sustainable conversion of lignocellulosic biomass into value-added products as this approach addresses the problems of low efficiency, high operational cost, and high energy consumption in different conversion processes of lignocellulosic biomass. However, there are a few limitations that narrow down the possibilities and contribute to the inapplicability of this approach at commercial scale. These challenges include high capital cost, biorefineries being limited to a single biomass type or biomass product, irregular supply chain of biomass, and each conversion process having its bottlenecks, making scaling-up difficult [11,144].

5. Future Prospects and Conclusions

Integrating biorefineries is the savior for accomplishing a cost-effective and sustainable supply of bioenergy. Therefore, progress can be continued by targeting a few objectives: (1) developing new, cost-effective technologies for the conversion of biomass; (2) effective engineering of the existing technologies to minimize energy consumption and increase their productivity; (3) lowering the carbon footprint by reducing the byproducts and waste

generated; (4) determining the complexities of the processes by studying the chemistry of biomass. In recent years, the plummeting price of crude oil has rendered biofuels less competitive. However, the future of biofuels is successful as fossil fuel supplies are shrinking day by day, and the demand for sustainable energy sources is sprouting.

Introducing cost-effective technologies is the most pressing need for sustainable energy generation. Devising new technologies or integrating more than one existing technology would utilize byproducts and waste as other usable energy sources such as thermal energy. This not only reduces the carbon footprint but also minimizes the burden on the environment. However, a thorough study of the processes and the characteristics of different lignocellulosic biomasses is necessary.

Commercializing biorefineries in the future is the tip of the iceberg. As renewable energy produced from a singular technology is expensive, consolidating these technologies at a commercial scale would sum up the output of renewable energy, making it economically viable. Extensive research is in progress regarding the integration of biorefineries to scale up the projects to fill the gap between the production and commercialization of biofuels and products.

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