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Chemically Pretreated Biomass Conversion for Biorefinery: A Review of Current Trends

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Abstract – The need for clean, alternative energy sources has increased due to the depletion of fossil fuel reserves and rising energy consumption. Saccharification, fermentation, and chemical pretreatment can turn lignocellulosic biomass (LCB), an affordable and renewable resource, into bioenergy potential. Chemical pretreatment is essential to convert LCB into biofuels or biochemicals in later stages. Certain upgraded pretreatments are required to improve LCB accessibility and digestion. Enhancing the hydrolysis of its carbohydrates, such as cellulose and hemicelluloses, is the inevitable of the LCB pretreatment. In order to produce bioproducts, lignocelluloses must have their refractory structure modified. Different pretreatment techniques have been developed to produce bioenergy from LCB. The most current developments in acid, alkaline, organosolv, deep eutectic solvents (DESs), and wet oxidation chemical pretreatment techniques (CPT) are reviewed and discussed. The study aims to increase our understanding of these pretreatment procedures and their potential as environmentally friendly technologies for advancing contemporary biorefineries and the future recommendations were discussed.

Key words: Biorefinery, Bioenergy potential, Ligno cellulosic biomass, Pretreatment technology, Upgrade chemical methods

1. Introduction

Energy consumption is predicted to rise roughly 28% by 2040 compared to current levels [1]. Presently, around 85% of the world's energy demands are met by petroleum-derived fuels. Acid rain, melting glaciers, global warming, greenhouse gas emissions, and deteriorating air quality are few of the environmental problems exacerbated by this excessive reliance [2]. Therefore, it is imperative to investigate alternate renewable energy sources. Eco-friendly energy is a major problem in developing nations, and renewable energy technology offers viable answers to future energy shortages and environmental issues [3]. By 2050, renewable sources are expected to supply about 85% of energy needs due to the projected significant increase in renewable energy output [4].

The main renewable energy sources for producing electricity include biomass, solar, hydro, and wind. Amongst various alternative and clean energy sources, bioenergy stands out owing to its carbon neutrality, versatility, and potential for continuous energy generation [5]. Bioenergy may reduce waste by using forestry and agricultural wastes to produce steady, dependable power, unlike intermittent sources are solar and wind. According to projections, bioenergy may account for 20–30% of the world's energy supply by 2050, which would be essential to reaching net-zero emissions. Its capacity to generate power, heat, and biofuels, as well as its integration with the current energy infrastructure, solidify its status as a crucial component of the energy mix of the future.

Agricultural residues can be classified into field-obtained residues (example: straw) and process-based residues (example: husk), which are typically generated in substantial quantities annually and often subjected to combustion or disposal [6]. The plant cell walls of LCB exhibit inherent recalcitrance to biochemical and enzymatic degradation, posing a significant challenge to the efficient valorization and bioconversion of lignocellulose feed stocks [7]. Bio-based products exhibit a reduced environmental footprint compared to conventional alternatives, making them integral for mitigating overall emissions and enhancing sustainable energy systems, thereby facilitating the transition towards a more environmentally responsible society [8]. Despite the numerous advantages of lignocellulose bio-refineries, the efficient valorization of LCB remains highly challenging due to its intricate structural composition and inherent recalcitrance to biochemical and enzymatic conversion [9].

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Cellulose, hemicellulose, and lignin constitute a majority of plant material called lignocellulosic biomass (LCB) [10]. These elements give plants their rigidity and resistance to deterioration. Together with each other, they create their structural framework [11]. The main elements of LCB, a plentiful and renewable resource, are the aromatic polymer lignin and the polysaccharides cellulose and hemicellulose [12]. LCB is divided into many categories, including aquatic biomass (algae, water hyacinth, and water weed), forest products (logging residues, wood, bushes, and shrubs), and agricultural leftovers (wood wastes, agricultural wastes, urban garbage, and crop residues) [13]. When used incorrectly, LCB can lead to soil and groundwater pollution, resource waste, and significant environmental issues [14]. Thus, it is essential to develop effective techniques for using LCBs in energy production [15]. LCB is regarded as a cheap, plentiful, and renewable natural resource that can produce several forms of bioenergy, such as bioethanol, biomethane, and biohydrogen. About 120×10^9 tons per year, equivalent to 2.2×10^{21} Joules, are produced annually worldwide in LCB, more than 300 times the world's present energy consumption [4].

Utilising LCB to create biofuels has garnered attention in recent years. Global biofuel production from LCBs can produce 15–20 billion metric tons of fuel annually [16]. The use of lignocellulosic wastes in commercial biofuels is growing [17,18]. Interestingly, most of the energy extracted from LCB is carbon neutral and produces nearly no greenhouse gas emissions [19]. Biofuels have the potential to drastically reduce the reliance on fossil fuels and the severe pollution that results from their burning [20]. Reducing greenhouse gas emissions from LCB could be achieved by producing biofuels and commercial bioproducts [21]. Furthermore, bioenergy generation from LCB can boost rural economies by generating new revenue streams, employment possibilities, and energy security [22].

Effective lignocellulosic biomass valorisation into biofuels is contingent upon the characteristics of the chosen raw material biomass and the kind and attributes of appropriate biological and non-biological pretreatment processes [23]. However, the LCB structure restricts how well it may produce biofuel. The pre-treatment of LCB is a crucial prerequisite to enhance the cellulose digestibility by selectively removing hemicellulose and/or lignin or modifying their structural arrangement within the cell wall, thereby improving cellulose accessibility for enzymatic hydrolysis [24]. The pre-treatment of LCB through various strategic approaches is a critical phase in its bioconversion into value-added bio-products, as well as in altering its recalcitrant structural matrix to enhance process efficiency [25]. The primary objectives of pre-treatment are to reduce cellulose crystallinity, enhance the surface area of biomass, facilitate hemicellulose recovery, and disrupt the lignin barrier in LCB, thereby improving its susceptibility to enzymatic and biochemical conversion [26]. Non-edible plants grown on non-agricultural lands offer a low-cost alternative that avoids both direct and indirect competition with land and food resources. There is a debate that first-generation (1G) biofuels should not be produced from crops that could be better used as food [27]. The food vs. fuel issue makes it impractical to produce 1G biofuels [28]. For example, coconut oil, groundnut oil, and sesame oil all of which are widely used in cooking, serve as first-generation feedstocks, and their use as fuel can have significant impacts on local food markets [29]. The main benefits of 1G fuel are low GHG emission and minimal investment cost of biomass to bioenergy conversion.

Second-generation (2G) biofuels are highly recommended since they can replace fossil fuels and cut greenhouse gas (GHG) emissions by 20–70% [1]. These biofuels from non-edible feedstocks include *Calophyllum inophyllum*, *Agle marmelos*, and *Azadirachta indica*. Since 2G biofuels are derived from non-edible sources, their use is often considered more ethical [30]. The pros of 2G fuel include the independence of food crops, ecofriendly fuels and reduction of carbon emission. The cons of 2G fuel are insufficient conversion technology, high investment cost for fuel production and stability of the fuel is poor. Waste agricultural leftovers, such as castle non-edible neem de-oiled cake, *Jatropha curcas* pressed seed cake, chicken fat oil, Agle *marmelos* de-oiled seed cake, and all types of algae species are used as source materials for third-generation (3G) biofuels [31,32]. Additionally, using byproducts from organic materials that are already part of the food chain presents a more promising strategy. These waste materials, typically low in moisture and high in carbon, are often incinerated or discarded [33]. However, their affordability, availability, and environmental benefits make them ideal for biofuel production [34]. The main advantage of 3G fuel is that it does not require arable land for feedstock materials production like microalgae biomass that can easily grow into waste and seawater. The disadvantage of 3G fuel is that the initial investment cost is high and requires high energy input. The fuel derived from genetically modified organism-based feedstock is known as fourth-generation (4G) biofuel, but it is still under development [35]. The pros of 4G fuel are high production yield and reduction in carbon emission and the cons of 4G fuel is the need for a high investment cost for bioenergy production.

The three primary constituents of lignocellulosic biomass are cellulose ($C_6H_{10}O_5$)n, hemicellulose ($C_5H_{10}O_5$)m, and lignin ($C_{10}H_{11}O_{3.5}$), with trace amounts of additional organic substances like pectin and protein [36]. Enzymatic hydrolysis can transform cellulose and hemicellulose into reducing sugars, which can be further processed into different chemical compounds [37]. Depolymerisation and hydrogenation can convert lignin, a heterogeneous polymer feedstock, into alkanes. Nevertheless, the conversion of lignocellulose is restricted by the indigestibility of lignin, its highly organised hydrogen bonds, and its complicated polymer structure [38]. Therefore, lignocellulosic biomass pretreatment is required and has been well-researched for practical purposes. Pretreatment is generally considered to entail modifying the lignocellulosic structure of the plant cell wall to improve the efficiency of enzyme access to the carbohydrate polymers for further processing [39]. Pretreatment of LCB improves bioconversion yield, biocompatibility, and enzyme accessibility [40].

This paper presents a comprehensive review of recent advancements

in various LCB processing and utilization strategies, focusing on different chemical pre-treatment methods. The latest technological developments in acid, alkali, organosolv, ionic liquid, deep eutectic solvent, and wet oxidation pre-treatment techniques are systematically analysed. This review aims to provide an up-to-date assessment of research progress (primarily from 2020 to 2024) on the conversion of LCB into biofuels, platform chemicals, and bio-based products.

Numerous pretreatment techniques have been used to overcome the resistant nature of LCB [41]. Pretreatment typically removes the lignin from the hemicellulose and cellulose in the complex structure. Therefore, efficient, cost-effective, and ecologically friendly pretreatment methods are crucial for LCB to be turned into bioenergy potential [42]. Pretreatment of LCB remains a significant area of research and development due to the importance of biomass resources and the limitations of existing technologies. Researchers are also exploring other strategies, such as enhancing plants to reduce lignin content and engineering microbes to tolerate various inhibitors. Although LCB pretreatment technology has been the subject of numerous review publications, most concentrate on broad overviews rather than in-depth examinations of the most recent developments in CPT. This review aims to give a thorough and in-depth analysis of the most recent advancements in CPT of LCB, within this framework. Researchers will receive constructive information about recent developments in chemical pretreatment methods from this review.

2. Components and composition of LCB

The biomass source determines the composition of LCB, which is further affected by climate, origin, age, season, harvesting, and storage methods [21]. The main components of LCB are carbohydrate polymers, which include 15-20% hemicelluloses, 35–45% cellulose, and 20–30% lignin [43,44]. Pectin, proteins, and extractives such waxes, non-structural sugars, and chlorophyll are also present in trace levels [10]. The amounts of lignin, hemicelluloses, and cellulose differ amongst plant species.

Different biomass sources have various compositions of cellulose. Whereas hemicellulose is a complex, amorphous polymer containing xylose as its main constituent, cellulose is a crystalline glucose polymer [45]. One sizable polyaromatic substance is lignin. A small quantity of ash and other extractives are also present in LCB [46]. LCB resists chemical and biological deterioration partly due to its rigid and complicated structure [16].

2-1. Cellulose

The biomass comprises cellulose, which forms linear homopolymer chains of 100 to 140,000 units, each of which is made up of cellobiose, a glucose disaccharide [4]. The structure of cellulose, a linear polymer made up of D-glucose units joined by β-(1-4) glycosidic linkages, is depicted in Figure 1(a-b). Microfibrils comprise these cellulose polymers joined by hydrogen and van der Waals connections. These can be crystalline or amorphous. 20 to 300 microfibrils held together by hydrogen bonds, covalent bonds, and van der Waals forces make up cellulose fibers [21]. Microfibrils are covered in lignin and hemicellulose. The non-covalent hydrogen bonds hold crystalline cellulose fibers together. They are three to thirty times less biodegradable than their amorphous counterparts [16]. Hydrogen bonding between lateral fibers is made easier by the number of hydroxyl groups, which improves structural stability. Hydrogen bonds between various chains decide whether the cellulose structure is amorphous or crystalline, while hydrogen bonds inside microfibrils guarantee the linearity of the homopolymer chain [47].

2-2. Hemicellulose

Hemicelluloses, which have a degree of polymerisation ranging from 200 to 700, are the second most abundant component in biomass. Xylan is the main structural component and comprises different combinations of monomers such as pentoses, hexoses, and sugar acids [10]. The branching structure and acetyl groups of hemicellulose is amorphous and does not form a crystalline structure [13]. This makes it easily broken down. Hemicellulose's structural makeup is depicted in Figure 2(a-b). It is easier to hydrolyse and remove under milder reaction conditions than cellulose [47]. Hemicellulose, which is non-covalently bonded to cellulose strands, functions as a matrix component in LCB. It is more prone to physical, chemical, and biological

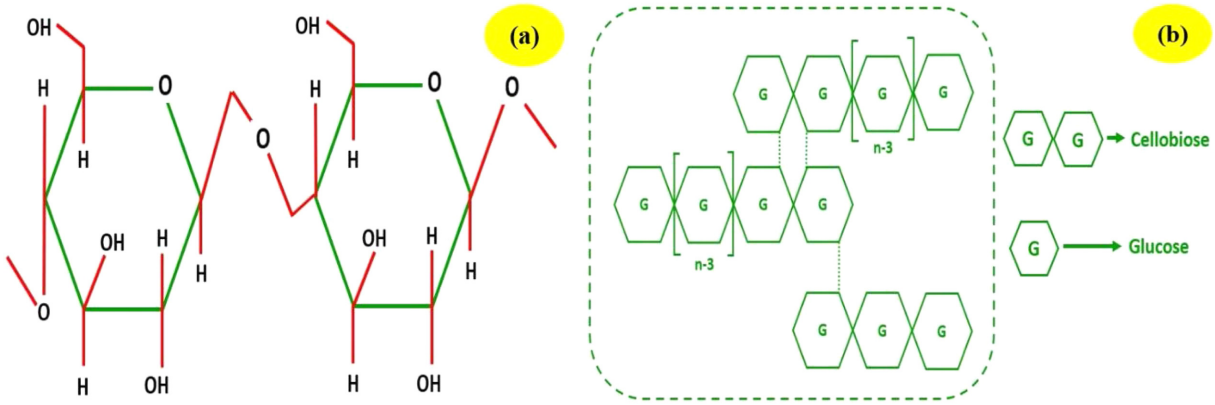

Fig. 1. (a-b) Schematic diagram of cellulose component structure.

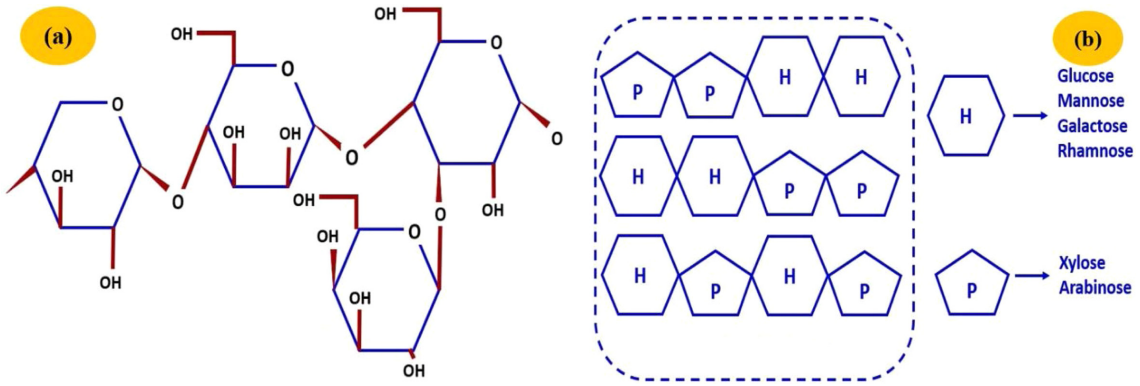

Fig. 2. (a-b) The edifice of hemicellulose with their components.

deterioration than cellulose due to its amorphous structure and lower degree of polymerisation [4]. Cellulase accessibility to cellulose is restricted by hemicellulose, a physical barrier. Enzyme addition and pretreatment techniques for hemicellulose removal improve cellulose hydrolysis [21]. Furthermore, the hemicellulose fraction adds stiffness to the overall biomass structure by binding the cellulose and lignin fractions together [48].

2-3. Lignin

15–30% of the biomass weight is made up of lignin, a polymer that gives plants their stiffness, impermeability, and microbial resistance [38]. The structure of lignin, an intricate amorphous polyphenolic polymer made up of three o-methoxylated p-hydroxyphenylpropanoid units [42], is depicted in Figure 3. Within the lignin polymer, these units aid in the synthesis of the p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) subunits [21]. Lignin is a binder for cellulose and hemicellulose fibers, giving them resistance to microbial invasions, mechanical strength, and assistance in developing vascular tissue to transport nutrients [47]. The lignin is hydrophobic, it can fill the voids left by cellulose and hemicellulose structures in lignocellulosic biomass, creating a physical barrier that prevents biological degradation [4]. However, the lignin prevents enzymes from interacting with the cellulose structure during hydrolysis, it presents difficulties in synthesising ethanol [16]. Consisting of sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol, lignin is a three-dimensional macromolecule. These monolignols are connected by C-O-C and C-C links, respectively [49]. They are also called the S, G, and H units. The chemical composition, binding force and composition percentage of LCB in different feedstock materials is shown in Tables 1 and 2, respectively.

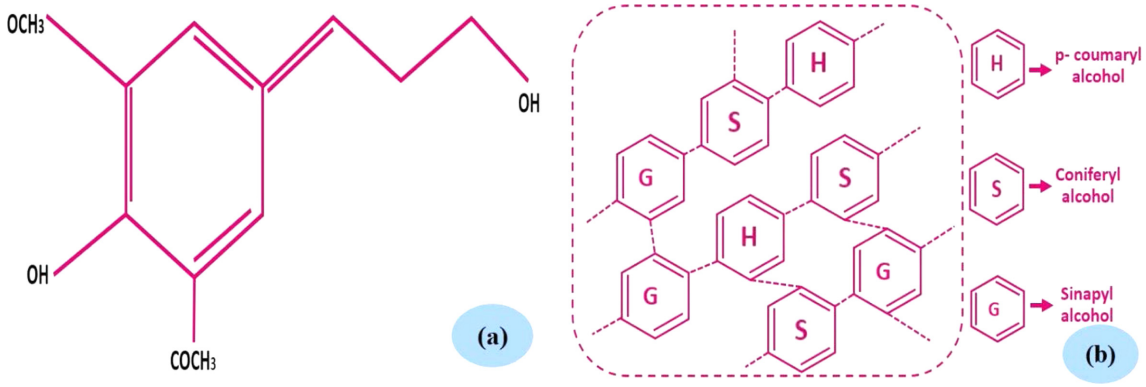

Fig. 3. (a-b) Construction diagram of lignin component.

Table 1. Chemical composition, binding force and structure of lignocellulosic biomass

Parameters	Lignin	Hemicellulose	Cellulose
Structure	Amorphous, non-uniform, nonlinear, 3D polymer	Few crystalline areas, A majority is amorphous area	Crystalline and amorphous area
Unit of structure	Syringyl, Guaiacyl, Para-hydroxy-phenyl	D-xylose, Mannose, Galactose, L-arabinose, Glucuronic acid	D-Glucopyranose
Structural unit of bond joint	C–C, R–O–R′	β-1.4-Glycosidic linkage	β-1.4-glycosidic linkage
Force between bond	Chemical bond	Chemical bond	Hydrogen bond
Polymer	G-, GS-, and GSH-type	Glucomannan, Galactoglucomannan, Xylan	β-1.4-Glucan
Level of polymers	4000	≤ 200	1000-10,000

Table 2. Composition of various lignocellulosic biomass

Biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Reference
Sugarcane bagasse	17	27	43	[10]
Soft wood	30	40	30	[16]
Corn stalk	30	20	50	[10]
Hard wood	25	50	25	[16]
Wheat straw	18.80	29.68	35.69	[50]
Bean straw	9.7	23.9	31.1	[45]
Switch grass	31.2	25.0	31.8	[51]
Banana pseudo	5.5	18.2	33.3	[52]
Corn stover	10.07	31.08	32.75	[49]
Sugar cane	22.34	22.95	37.2	[53]
Rice straw	19.55	27.59	38.82	[54]
Olive tree	24.1	21.3	36.5	[55]
Bamboo	29.3	18	41.8	[56]
Grasses	15	50	35	[16]
Water hyacinth	8.6	34.1	24.5	[10]

3. Overview of the Pretreatment Methods

Pretreatment is an important stage in the energy conversion process because it makes the complicated components of LCB easier to separate or solubilise. The organisms, enzymes, and compatibility of the feedstock material should all be considered when selecting a pretreatment [16]. Pretreatment techniques can be broadly categorised into physicochemical, chemical, and physical [10]. The advanced CPT techniques for LCB are shown in Figure 4. In order to expose the cellulose and hemicellulose content for hydrolysis using chemical, enzymatic, or other methods, pretreatment is necessary [21]. Different kinds of LCB and pretreatment techniques influence the efficiency of pretreatment and the ensuing conversion of biomass. Studies have indicated that lignocellulose with a lower lignin content is more affected by acid-base pretreatment [57]. To date primary pretreatment difficulties centre on comprehending the mechanisms underlying the different forms of LCB.

A critical and inevitable step in the bioconversion of LCB to bioenergy and in changing its resistant structure is the pretreatment of LCB utilising various techniques [4]. The internal effects of chemical pretreatment on the structure of LCB are depicted in Figure 5. Pretreatment's main goals are to break down the lignin barrier in LCB, recover cellulose, enhance biomass surface area, and decrease cellulose's crystallinity [11]. Hemicellulose and lignin extraction from LCB reduces biomass recalcitrance and yields a solid residue with a high cellulose concentration [58]. The key factors influencing the reaction during and after the LCB chemical pre-treatment are the high concentrations of several catalysts, including ionic liquids, acids, and alkali [28]. To increase enzyme accessibility to cellulosic fibers, researchers have created a variety of pretreatment strategies in recent years [46], including physical, chemical, biological, and combinational approaches. Each technique has unique benefits and drawbacks depending on the substrate type and pretreatment settings [13]. Table 3 lists the benefits and drawbacks of sophisticated chemical procedures.

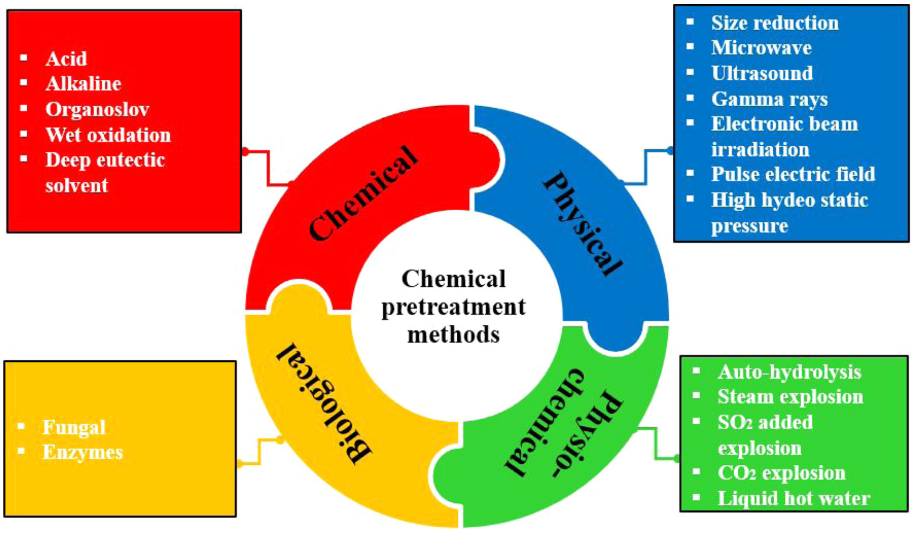

Fig. 4. Classification of pretreatment methods of lignocellulosic biomass.

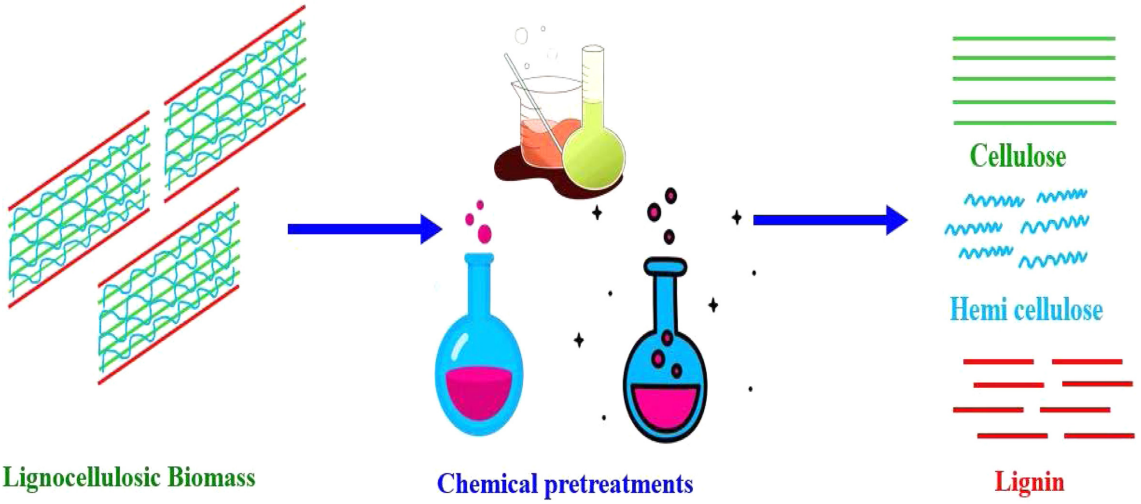

Fig. 5. Structure and impact of chemical pretreatment on lignocellulosic biomass.

Table 3. Pros and cons of current chemical pretreatment methods

Pretreatment Technology	Pros	Cons
Alkaline pretreatment	The extraction of lignin is well systematic one.	Chemical cost is high
	Generation of inhibitors is null	Low sugar degradation
	Room temperature process	Residence times is long
	Eradicated the lignin	Energy consumption rate is high
	Production of inhibitors is less	Environmental pollution
Acid pretreatment	Maximum value of sugars extraction	Cost of the acid is high
	Solubilise hemi-cellulose	Not possible of recycling and reuse of chemicals
	Reaction time is short	Corrosion is inevitable process
		By-product may produce
		Toxicity is high
Ionic liquid	Processing capability is higher	Ionic liquid cost is high
	Room temperature reaction condition	Solvent recovery and recycle is essential
	Environmental process	
Organoslov	Condition of cellulose is active	Ethanol is acted as inhibitor
	Recyclable solvents	Rate of energy is very high
	Catalyst is not required	Certain effects the fermentation and environment
	Attained pure lignin, cellulose, hemicellulose	Corrosive rate is high
	Low reaction time	Toxicity
Wet oxidation	Cost of oxidants (O_2) is less	Process cost is high
	Deconstruction of LCB cell wall efficiency is high	Scale up issues
	Low inhibitors formation	Create corrosion in equipment
	Reaction times is short	High energy consumption
	Produce valuable products	
	Enhanced biodegradability	

Table 4. Major outcomes of upgraded chemical pretreatment technologies

Parameters	Acid	Alkaline	Ionic liquid	Organosolv	Wet oxidation
Surface area	Increase	Increase	Increase	Increase	Increase
Crystallinity	Decrease	Decrease	Decrease	Decrease	Decrease
Delignification	High	High	Low	High	High
Major outputs	Hemicellulose converts into sugars	Hemicellulose and lignin separation	Lignocelluloses residues solubilisation	-	Exclusion of hemicellulose and lignin
Chemical usage	H_2SO_4, HCl, H_3PO_4	NaOH, NH_3, KOH, NH_4OH, Ca $(OH)_2$	Ionic liquid	-	H_2O_2, O_2, O_3 (Oxidizing agents)
By products/Inhibitors	Carboxylic acid, Aliphatic and Phenolic compounds	Acetic acid, Hydroxyl acid, Phenolic compound, Carboxylic acid	Depends on solvent	-	Furans, Phenolic and aliphatic compounds

Table 4 provides a comparative study of a few contemporary chemical pretreatment techniques for LCB.

4. Essential of Pretreatment of Biomass

The recalcitrant nature of LCB is a key barrier to its utilisation in biorefineries and offers a considerable technical challenge for releasing fermentable sugars from the biomass [21]. The innate ability of plant cells to withstand attacks by animals, environmental factors, and microbial deterioration is known as LCB recalcitrance [3]. Recalcitrance is influenced by the structural elements of lignin and hemicellulose and other elements such as biomass porosity, acetyl groups, and proteins. This property acts as a barrier to the industrial use of LCB, requiring alternative pretreatment techniques to get around the problem [21].

A crucial pretreatment process is required to break down lignocellulosic biomass and its effective conversion to bioenergy [16]. During the pre-treatment phase, altering the inherent structure of LCB components is crucial. For example, during delignification, lignin's original structure is typically changed to make it more valuable. Furthermore, decreasing the cellulose fraction's crystallinity during pre-treatment increases the enzymes accessibility [4]. When creating the ideal pretreatment strategy, it is important to consider the complexity and unpredictability of LCB to ensure each component's composition and structure are not adversely affected [10].

5. Chemical Pretreatments

Chemical pretreatment is the process of dissolving the hard lignocellulosic biomass structure and separating its constituent parts using particular chemicals [13]. This process increases biomass conversion and produces higher bioenergy outputs by dissolving the resistant LCB components such as cellulose, hemicellulose, and lignin using a variety of chemical agents [59]. Alkali, oxidation, organic solvent, and acid pretreatments are efficient methods for enhancing lignocellulose's biodegradability, boosting its surface area, and changing its crystalline structure [28]. Various CPT techniques seek to transform LCB feedstock into optimal substrates for the synthesis of biofuels [60]. Extensive measures are implemented to mitigate or prevent the development of harmful inhibitors that may impact subsequent procedures and diminish the yield of bioenergy [10]. The following discussion reveals recent developments in lignocellulose chemical pretreatment.

5-1. Acids Pretreatment

The LCB was acid-pretreated to improve the enzymes accessibility to cellulose. The covalent bonds, hydrogen bonds, and van der Waals forces holding the LCB components together were broken by this treatment [31]. Its main job was to extract and segregate lignin and vegetal fibers so that cellulose and hemicellulose may hydrolyse more easily. During this process, cellulose, a kind of hexosan, and hemicellulose, which was primarily made of pentosans, underwent hydrolysis [4].

Reagents like sulfuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl) were frequently used for acid pretreatment [16]. Aqueous sulfuric acid (H_2SO_4) was frequently used to pretreat several kinds of LCB [3]. Pure sulfuric acid was first diluted to produce furfural by turning hemicelluloses into sugars, which were then turned into furfural [31]. There are two types of acid pretreatment: one used concentrated acid with concentrations between 30% and 70% at relatively lower temperatures below 100℃ for not more than two hours at ambient temperature, and the other used dilute acid with concentrations less than 10% at temperatures above 200℃ [16]. LCB was treated with concentrated acid to produce cellulose dextrin, which increased its hydrolysis susceptibility, albeit at a rather slow rate [59].

On the other hand, continuous production can be achieved by the quick reaction process of dilute acid treatment, eliminating the need for acid recycling. Nevertheless, the fermentation of lignocellulose was adversely affected by the breakdown products that occurred due to unusually high temperature and pressure requirements of this method. In addition, the acid needed a long time to neutralise before sugar fermentation can begun, and even with a high energy input, its lignin-removal capacity was limited [16]. Every acid pretreatment technique had benefits and drawbacks of its own. The diluted acid pre-treatment involved greater temperatures, it used more energy even if it consumed less acid [23]. Conversely, intense acid pretreatment lowered reaction temperatures and hence energy consumption; however, the increased acidity caused fermentation inhibitors to be produced [57]. These inhibitors harmed the microbes that were employed in the fermentation process. They broke down Deoxyribonucleic acid and reduced the synthesis of Ribonucleic acid, which inhibited enzymatic activity [61]. Temperature, lignocellulose concentration, duration, and acid concentration all directly impact how well an acidic pretreatment works [13]. Inhibitors such as 5-hydroxymethylfurfural and furfural can be produced, equipment can corrode, and fermentable sugars can be lost as a result of higher acid concentrations and longer pretreatment durations [10].

The production of inhibitory chemicals like furfural, equipment corrosion from strong acids, sugar degradation, ineffective lignin removal, and challenges with acid recovery and neutralisation were the primary R&D issues in acid pretreatment of LCB. Researchers are employing detoxification techniques (such as adsorption and enzymatic treatment), utilising alternative acids, optimising process conditions, and incorporating bio-refinery technologies to increase overall efficiency in order to overcome these obstacles. Lignin valorisation was also being investigated to improve the process's economic viability.

5-2. Alkaline pretreatment

One of the most well-known methods for lignin removal or redistribution and biomass mercerization was alkaline pretreatment. Compared to other techniques (such as acid pretreatments), alkaline

pretreatments were more manageable since they typically involve mild reactions, alkaline chemicals are recoverable and reusable, and they offer a high selectivity for lignin extraction [62-64]. Pretreatment was done to reduce the processing cost of lignocellulosic biomass by making it susceptible to enzymatic reactions, or saccharification. A few frequently noted results of pretreatment consisted of reducing the biomass's lignin concentration, increasing its surface area, and decreasing its crystallinity; these actions all raise the rate and yield of enzymatic hydrolysis. Alkaline pretreatment approaches using diverse chemicals have been researched to enhance enzyme digestibility of lignocellulosic biomass [65,66]. The major categories of chemicals used in this regard were sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), ammonia (NH_3), and calcium hydroxide ($Ca(OH)_2$) etc.

Alkaline pretreatment (APT) compounds tend to be less harsh than their acidic counterparts. This process involved soaking in sodium or ammonium hydroxide under milder circumstances, such as ambient temperature. This approach minimized the need for costly materials and specialized designs to withstand corrosion and harsh reaction conditions. Some alkaline pretreatment procedures also allowed for chemical reagent recovery and reuse [67]. The main effect of alkaline pretreatment was cell wall disintegration, which was accomplished by breaking down polysaccharides and causing chemical swelling. This broke down the connections between lignin and carbohydrates and eventually removed lignin. Consequently, this raised the biomass's surface area and porosity while lowering the level of polymerization. These modifications improved structural carbs' reactivity and susceptibility to enzymes, which made it easier for them to be converted to fermentable sugars [68].

Pretreatment with sodium hydroxide has been studied since the start of the 19th century to improve cellulose digestion by ruminant animals. This powerful base can substantially dissolve hemicellulose and lignin in certain conditions making pretreatment more effective. In particular, sodium hydroxide cleaved the ester and ether bonds in the lignin-carbohydrate complex (LCC) structure, thereby attacking the coupling between lignin and hemicellulose. The breakage of ester and carbon-to-carbon (C–C) bonds in lignin molecules (ferulic acid) can also be accomplished with sodium hydroxide. Sodium hydroxide separated into hydroxide ions (OH) and sodium ions (Na+) during the NaOH pretreatment reaction. The rate of the hydrolysis reaction raised in proportion to the quantity of hydroxide ions [65].

The authors of a study pretreated the sweet sorghum bagasse (SSB) and corn cob (CC) biomasses with NaOH and $CaOH_2$ in an effort to remove lignin from them. The effectiveness of each pretreatment on the biomass was then assessed. When pre-treating CC biomass, alkaline pretreatment proved to be more successful than SSB biomass. Lignin was extracted from the CC biomass by both the $Ca(OH)_2$ and NaOH pretreatments, however it was only extracted from the SSB biomass by NaOH. The chemical composition of these agrarian raw materials varied, according to a biomass compositional analysis, with CC biomass having hemicellulose (33–35%) as its principal component and SSB biomass mostly consisting of cellulose (17–24%) [69]. In another case, following an alkaline pretreatment with NaOH, Napier grass showed a notable rise in cellulose content and a large drop in lignin concentration. The treated sample's cellulose content grew to about 61.7%, while in another work the sample's cellulose content increased up to 97% based on the NaOH concentration. Similarly, the removal of hemicellulose and lignin contents was found to be 30% and 22% respectively [70]. Studies by researchers have shown that alkaline pretreatment can also raise the hemicellulose content. This rise could be explained by a large loss of lignin, which raised the relative amount of hemicellulose [71]. Researchers also reported that when compared to acid pretreatment, the alkaline pretreatment of the biomass produced better results, particularly for hybridized feedstocks where the concentration of sulfur was lower [72].

Na_2CO_3 has similar pretreatment efficacy to other alkaline reagents. Na_2CO_3 pretreatment can remove lignin and different uronic acid replacements in hemicellulose, but caused less cellulose degradation than acid or hydrothermal pretreatments [67]. Some researchers have aimed at treating corn stover, a waste from agriculture residue with 2.2 M Na_2CO_3, derived from CO_2 collected through absorption in a 5 M NaOH solution. The chemical composition analysis of the treated biomass revealed a higher cellulose content (40.96%) and less lignin (16.50%) than the untreated biomass. The pretreatment phase accelerated lignin decomposition, lowering it by 35% while boosting cellulose content by 18% [73]. Another study investigated the effects of moderate Na_2CO_3 pretreatment on the enzymatic hydrolysis of various feedstocks, including corn stover, miscanthus, and switchgrass. The pretreatment effectively reduced the recalcitrance of the biomass substances. The outcome of pretreatment was the elimination about 60% lignin and 14% xylan, while retaining the majority of cellulose components [74].

Ammonia-based pretreatments have been intensively researched over the past few years as one of the most effective pretreatment strategies for lignocellulose biorefining. One of the first forms of soaking in aqueous ammonia (SAA) pretreatments described in the literature was for the production of bovine feed, which was later modified to produce pretreated feed for cellulosic biorefineries [75]. A recent investigation examined the impact of integrating ozone and SAA-based pretreatments (OSAA) for rice straw. The optimum OSAA pretreatment parameters for rice straw were 90 minutes of ozonation and 9 hours of SAA treatment, which increased the generation of biogas by about 58%. In general, the initial SAA pretreatment failed to account for either ammonia or hemicellulose retrieval. It was ought to be pointed out that for industrialized SAA pretreatment, there should be a greater emphasis on ammonia recycling and reuse [76]. Shi et al. recently invented a pretreatment solution that utilized aqueous ammonia and glycerol mixture (AAWG), with an emphasis on ammonia retrieval. Their findings revealed that soaking sugarcane bagasse (SCB) in an AAWG solvent mixture at 180℃ for about 2 hrs resulted in 71% lignin removal and 0.45 g/(g biomass) total fermentable sugar yield. Further, approximately 30% of the ammonia was extracted from the

pretreatment liquid *via* distillation. As a result, AAWG could function as an economical large-scale commercial biomass pretreatment technology [77].

$Ca(OH)_2$, like NaOH, is commonly employed in lignocellulosic material pretreatment. $Ca(OH)_2$ was a more economical reagent than NaOH and did not impaired anaerobic digestion [78]. A study found that applying a $Ca(OH)_2$ pretreatment could considerably increase the extruded rice straw biogas generation rate and enzymatic hydrolysis efficacy. Following the processing, the physical and chemical properties of the extruded rice straw changed, resulting in improved biological degradation. Positive benefits were seen at all $Ca(OH)_2$ loading rates; however, overloading $Ca(OH)_2$ resulted in increased fermented carbohydrate reduction, reducing overall generated biogas. The ideal $Ca(OH)_2$ dosage was 8%, which resulted in effective hydrolysis and substantial biogas yield [79]. The influence of hydrothermal (HTP) and $Ca(OH)_2$ pretreatments on the biogas generated by anaerobic degradation of SCB was investigated by Mustafa et al., where the HTP, $Ca(OH)_2$, and combined pretreatment had a substantial effect on hemicellulose and lignin decomposition, as well as methane output following digesting. Their findings showed that HTP prior to $Ca(OH)_2$ pretreatment increased lignin and hemicellulose breakdown. Combining HTP with $Ca(OH)_2$ resulted in a 61.3% increase in methane yield compared to untreated SCB [80].

High chemical consumption, lengthy reaction times, partial lignin removal, and the production of by-products that may impede downstream processing were the primary R&D issues in alkaline pretreatment of LCB. Process expenses were further increased by the recovery and recycling of alkaline reagents like NaOH and KOH. Researchers are working to overcome these obstacles by enhancing reaction conditions, investigating substitute alkaline agents (such as lime and ammonia), combining pretreatment with enzymatic hydrolysis, and creating effective chemical recovery methods. Strategies for lignin valorisation are also being sought in an effort to increase the process's overall economic feasibility.

5-3. Organosolv pretreatment

The following organic solvents were frequently used in organosolv procedures or organic-aqueous solutions: ethylene glycol, methanol, ethanol, tetrahydrofuran, and acetone [10]. α-O-aryl, β-O-aryl, and 4-O-methyl glucuronic acid ester linkages (alkyl aryl bonds (α-O-4, β-O-4)) in lignocellulose can be broken by organosolv treatments [31]. This procedure pacified the enzymatic hydrolysis of cellulose to produce biofuels from sugars by facilitating the breakdown of hemicellulose and lignin [81]. Furthermore, bases like lime and NaOH or organic acids like oxalic acid, acetylsalicylic acid, and salicylic acid were occasionally used as catalysts in these procedures [82].

Hemicellulose and lignin linkages were broken down through solubilisation during this pretreatment procedure, increasing cellulose's total surface area available for enzymatic hydrolysis [31]. The cellulose content in the solid phase wa still active during this process. The methanol and ethanol have higher boiling points than tetrahydrofurfural alcohol and ethylene glycol, they was more desirable because continuous solvent recycling lowered costs [4]. Nevertheless, a significant disadvantage of these techniques was the ongoing requirement for solvent recovery, which raised the generation of biofuel's running expenses [13]. Furthermore, ethanol was an inhibitor and needed to be eliminated. As a result, a thorough washing was needed to remove the solvent from the processed biomass residue. For solvent recovery, liquid-liquid extraction or distillation techniques were usually used [16].

The high cost of organic solvents, the difficulties in recovering and reusing them, possible safety and environmental issues, and the partial removal of lignin were the primary R&D obstacles in the organosolv pretreatment of LCB. Furthermore, fermentation and enzymatic hydrolysis may be impeded by the existence of residual solvents. In order to overcome these obstacles, scientists are investigating biodegradable and reasonably priced solvents, refining solvent recovery methods, enhancing lignin removal through process optimisation, and incorporating lignin valorisation approaches to reduce expenses. Innovations in co-solvent and catalytic systems are also being researched to increase the sustainability and overall efficiency of processes.

5-4. Eco-friendly pretreatment methods

Technological developments have resulted into environment friendly pretreatment techniques that work extremely well with the fermentation and hydrolysis processes. These include new methods like pretreatment with ionic liquid and deep eutectic solvent [57].

5-4-1. Ionic liquids pretreatment

Owing to their special qualities, ionic liquids (ILs), cellulose solvents, are frequently referred to as "green solvents" [50]. These include the following: low vapour pressure needs, easy accessibility, the high recovery efficiency of up to 99%, non-explosiveness, high thermal stability, lack of harmful gas production, and low requirements for vapour pressure [83]. Typically, ILs are made up of big organic cations and small inorganic anions that combine to generate liquid organic compounds at low temperatures [84]. ILs extract pure cellulose from LCB, leaving hemicellulose and lignin behind for further hydrolysis. It is possible to continuously carry out ILs pretreatment effectively, which can handle more LCB input with better results [50].

Imidazolium-based ionic liquids, alkyl ammonium-based ionic liquids, phenol-based lignin-derived ionic liquids, and other ionic liquids have all been used for pre-treating LCB [83]. In the LCB pretreatment process, the main job of ILs is to dissolve and swell cellulose and lignin. The particular pairing of cations and anions breaks down β-O-4 bonds in lignin to generate ion-dipole bonds, which is the mechanism of interaction between ILs and lignocellulose [85]. This disrupted the crystalline structure of LCB [36], which in turn causes the lignin structure to break down and separate into hemicellulose and lignin from the cellulose components [13].

Cations based on imidazolium are frequently used to pretreat LCB. Imidazolium-based ILs pretreatment resulted in the conversion

of crystalline cellulose to an amorphous structure and the enhancement of phenolic hydroxyl groups in lignin [36], which lowered molecular weights and facilitated polysaccharide and lignin extraction and separation. Choline ionic liquids were an important class of ILs that eliminated lignin and other amorphous materials to increase the crystallinity of biomass [85]. Nevertheless, toxicity concerns, problems with pH compatibility, process complexity, and high cost were some of the disadvantages of ILs [21]. Moreover, their high viscosity made recycling more difficult [57]. Although imidazolium-based ILs have demonstrated notable results in LCB pretreatment [86], their practical uses were limited by their toxicity to enzymes and bacteria, which required thorough washing following pretreatment [81].

In addition, ILs pretreatment is currently one of the most emerging, promising, and eco-friendly strategies because of its ability to stay in the liquid state at temperatures below 100℃ [87]. Their specific chemical properties, such as low vapor pressure and high thermal stability, allow them to be extremely effective for the destruction of lignocellulosic biomass recalcitrant structure, thereby efficiently dissolving the cellulose, hemicellulose, and lignin components [88,89]. The tunable nature of ILs can achieve the selective dissolution of lignin and hemicelluloses while preserving cellulose [90,91]. This selective disruption increases the surface area accessible to enzymes and allows for significantly enhanced hydrolysis to take place, thus increasing the yield of fermentable sugars critical to ethanol manufacturing. Several types of ILs such as ammonium, imidazolium, pyridinium, pyrrolidinium, tetrafluoroborate, methylsulfate, and phosphonium were studied for the efficient conversion of 1G to 4G lignocellulosic biomass. Among them, Imidazolium-based ionic liquids have been more studied for biomass pretreatment, due to their high efficiency in breaking the complex crystalline structure of lignocellulose. The combination of imidazolium cations with a variety of anions, such as acetate ($[OAc]^-$) or chloride (Cl^-), made these ILs quite capable of dissolving cellulose and lignin [92,93,94]. Their key role in processing biomass was to break hydrogen bonds within cellulose to made it more accessible during the hydrolysis to enzymes, therefore increasing the yield of fermentable sugars, which were quite important during biofuel production. The ILs mainly 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$) and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), were effective in dissolving lignin and cellulose that decreased the recalcitrance of biomass [95,96,97]. In this respect, imidazolium ILs have became recognized for these selective dissolution properties because they keep cellulose intact while dissolving lignin and hemicellulose for easier downstream processing [98].

The class of ILs that contains the ammonium cations is the ammonium-based ILs. These could be primary, secondary, tertiary, or quaternary, all of which give them the disruption power on lignocellulosic biomass. Much attention has recently been paid to these ammonium ILs because of their eco-friendliness, low cost, and strong solubilization capabilities. Experiments have been conducted over newly synthesized ammonium ILs, and some of them, like N-Methyl-diethanolamine, showed the ability to deconstruct complex biomass structures [99]. Moreover, the rheological properties of the ammonium ILs, which made them very adaptable under extreme conditions of high temperature and pressure, for instance, would made them quite suitable for industrial application [100]. In phosphonium-based ILs, a phosphonium cation is combined with several anions such as acetate, chloride, or others, which boosts their performance in biomass pretreatment. Phosphonium ILs showed a great future in applications under very aggressive industrial environments because they were able to work at high temperatures and other challenging conditions. Among others, phosphonium ILs were known to be very effective in the solubilization of cellulose. Trihexyl(tetradecyl)-phosphonium acetate ([THTDP][OAc]) has shown great efficiency in the breakdown of structures that are lignocellulosic in nature, turning them very promising for large-scale biomass conversion operations. Besides, phosphonium ILs have good recyclability, which adds to their growing appeal in sustainable biomass processing technologies [101]. Another class of ILs belongs to choline-based ILs, which are known to be biodegradable and sustainable. They consist of a choline cation usually combined with different anions such as amino acids or acetate. Choline-based ILs have been getting attention for their application in biomass pretreatment due to the small impact they have on the environment, and they are often derived from natural, nontoxic sources. For instance, cholinium l-alaninate ([Ch][Ala]) was found to increase the deconstruction of lignocellulosic biomass while maintaining low levels of toxicity, hence finding an application in green chemistry approaches to bioenergy conversion. It also represented great value for these ILs to be cost-effective, most of the time originating from inexpensive materials such as choline chloride. The ability to recycle and reuse further enhanced their applicability in the realm of sustainable industry-related applications [102].

Among the subclasses of ionic liquids, protic ionic liquids (PILs) are built from a proton donor and a proton acceptor and are hence very effective solvents for biomass pretreatment. PILs are made via the transfer of a proton from a bronsted acid to a bronsted base and yield liquid salts with special hydrogen-bonding capabilities [103]. These properties render PILs efficient at breaking down the crystalline structure of cellulose and solubilizing lignin, hence presenting effective ways of the lignocellulosic biomass's rigid structure disruption. The hydrogen bonding in PILs allows the dissolution of cellulose and lignin while increasing the cellulose exposure for enzymatic hydrolysis. Examples such as ethylammonium nitrate were commonly used due to their increase in biomass breakdown and being relatively environmentally friendly. Other attractive features of PILs, which made them an exciting prospect from among several types of materials in this domain, included extremely low volatility and potential biodegradability, rendering PILs a much greener option than the traditional choices for solvents. They can also be formed from low-cost and easily available materials, thus offering the advantage of economic viability for large-scale applications of bioenergy.

On the other, the carboxylate-based ILs are generally attributed to

strong disruption of the crystalline structure of cellulose in LCB owing to the dissociative acidic nature of the carboxylate anions. Among ILs, the sulfonate-based ones are a specific class that has been reported to be effective in delignification during biomass pretreatment. ILs with the sulfonate anion have been found to demonstrate selectivity toward the dissolution of lignin, leaving cellulose and hemicellulose intact. For example, 1-ethyl-3-methylimidazolium methylsulfonate ($[C_2mim][MeSO_3]$) and 1-butyl-3-methylimidazolium sulfonate ($[Bmim][MeSO_3]$) are known to cleave the lignin network of LCB. These sulfonate anions complex with the lignin molecules to finally release the lignin from the biomass, increasing the enzymatic accessibility to cellulose. This selective dissolution can play an important role in increasing biofuel yield, as the hydrolysis of cellulose to fermentable sugars was done more efficiently. Further, sulfonate-based ILs can be used for many biomass processing applications because of their recyclability and relatively low toxicity toward sustainability. Great solvating ability coupled with low environmental impacts gave promising expectations in the development of their large-scale applications in the bioenergy sector. The optimized conditions for different ionic liquids used in the pre-treatment of LCB are given in Table 5.

The cost and toxicity of ILs, the difficulty of recovering and recycling them, and the process restricted scalability were the primary research and development obstacles associated with ionic liquid pretreatment of LCB. Furthermore, certain ionic liquids have the potential to degrade cellulose or obstruct further enzymatic hydrolysis. By creating more affordable, eco-friendly ionic liquids, refining solvent recycling methods, and increasing the process overall scalability, researchers are tackling these issues. To increase process sustainability and commercial feasibility, efforts are also being made to reduce cellulose degradation and boost enzymatic conversion efficiency.

5-4-2. Deep eutectic solvents pretreatment

Mixtures of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) with freezing temperatures lower than 100℃ are referred to as deep eutectic solvents (DESs) [124]. A eutectic mixture is essentially a homogenous combination of two or more substances with a particular composition ratio that melts and freezes at a temperature lower than the melting temperatures of its constituent parts separately [125]. Many common reagents used in industry today are hazardous to the environment. As a result, the demand to create substitute green solvents has increased. Over the past 20 years, DESs have attracted much attention due to their environmental friendliness [53].

Deep eutectic solvents were created in 2003 by Abbott et al., [126], by combining a HBD and HBA in particular ratios. DESs are more compatible with enzymes and microorganisms than ILs and traditional reagents [127]. Similar to ILs, one of their main advantages is

Table 5. Optimized conditions for the ionic liquid pre-treatment of lignocellulosic biomass

Biomass Type	Ionic Liquid	Temperature (°C)	Biomass Loading (%)	Time (min)	Yield (Ethanol or Reducing Sugars)	Reference
Rice straw	1-H-3-methylmorpholinium chloride ([HMMorph][Cl]) (water and dimethyl sulfoxide (DMSO) as co-solvents)	120	5	300	64% (Ethanol)	[104]
	Choline acetate ([Ch][OAc])	129.21	10.68	331.82	542.3 mg reducing sugar/g-biomass	[105]
	cholinium acetate ([Ch][OAc])	130	13.79	304.27	57.12 mg/0.1 g-rice straw	[106]
	1-butyl-3-methylimidazolium chloride (recycled)	120	5	60	91.9 g/L ethanol	[107]
	1-ethyl-3-methylimidazolium acetate ([EMIM][OAc])	120	5	300	75% glucose yield	[108]
	1- ethyl-3-methylimidazolium acetate (EMIM-Ac) + NaCl	160	7.6	88.7	670.7 mg reducing sugar/g biomass	[109]
	1- ethyl-3-methylimidazolium acetate (EMIM-Ac) + KCl	160	12.5	68.2	392.9 mg reducing sugar/g biomass	[110]
	1-ethyl-3-methylimidazolium acetate	120	5	300	298.8 g/L fermentable sugars, delignification (64.9%)	[111]
Corn cob	Tetrabutyl phosphorus hydroxide (TBPH)	60	6	90	90.75% sugar yield	[112]
Corn stalk	Tetrabutyl phosphorus hydroxide (TBPH)	80	7	60	80.84% sugar yield	[112]
Corn straw	1-ethyl-3-methylimidazolium acetate ([Emim]Ac)	98.5	11.49	78.6	Lignin removal 87.4%	[113]
Corn Stover	Levulinic Acid-Based PIL	140	10	40	0.8 g/g reducing sugar (delignification 44.3%)	[114]
Corn Stover	1-butyl-3-methylimidazolium chloride (C4mimCl)	130	5	120	96% glucose yield	[115]
Corn Straw	ethyl methanesulfonamide (EAM)	130	7	120	95% sugar yield, delignification rate 96%	[116]
Wheat straw	Triethylammonium hydrogen sulfate [TEA][HSO4]	130	20	30	42 g/L ethanol, 74.9% delignification	[117]
	Choline taurinate [Ch][Tau]	80	10	360	79.7% reducing sugar yield	[118]
Coconut waste	N,N,N-dimethylbutylammonium hydrogen sulfate ($[DMBA][HSO_4]$)	170	10	45	82% lignin removal and 89% glucose yield	[119]
Sugarcane bagasse	1-ethyl-3-methylimidazolium acetate ([EMIM]oAc)	145	14	15	69.7% reducing sugar yield	[66]
	1-ethyl-3-methylimidazolium acetate [Emim] [Ac]	120	5	120	98.2% glucose yield	[120]
	Triethylammonium hydrogen sulfate ($[TEA][HSO_4]$)	120	10	240	90% of the lignin removed	[121]
	N-methyl-2-hydroxyethylammonium acetate, $[Me(NH_2)(CH_2)_2OH]$ [OAc],	160	10	180	72% of glucose yield	[122]
Poplar wood	Triethylammonium hydrogen sulfate ($[TEA][HSO_4]$)	140	5	420	70.1 % lignin removal, 86.47% glucan yield	[123]

the wide tunability of their chemical and physical properties. Due to their special qualities, which include their high polarity and easy miscibility with water and other co-solvents, DESs have been widely used to delignify various LCB [57]. Ionic liquid analogues, or DESs, are a novel class of ILs that comprise HBAs (alanine, choline chloride, betaine, etc.) and HBDs (alcohols, urea, acids, amides, etc.) [13].

The hydrolysis of lignin-carbohydrate complex bonds was aided by the competitive hydrogen bonds between HBD and HBA with hydroxyl groups and carbohydrates in lignin [125]. It was interesting to note that DESs became less viscous as the temperature raised, improving mass transmission in the system [42]. Moreover, DESs can extract lignin from LCB complexes in a selective manner, providing a greener alternative to pretreat LCBs under mild reaction circumstances [10].

Recently, Deep Eutectic Solvents have gained attention as a potential pre-treatment for LCB, referring to their appropriateness for bioenergy application. Some of the most worrisome features of the use of ionic liquids and harsh chemical solvents were high cost, adversities to the environment, and toxic nature, among others [128]. They provided a potential alternative to the currently low-cost, biodegradable, less toxic, reduced cost in waste disposal, and low-corrosion feature of the currently limited number of DES that fits the sustainable bioprocessing approach. Largely, the development of the field of DES pointed to a way of handling chemicals in industries that was both economically and environmentally friendly. DES can be mainly composed of two or more components, most often a HBD and a HBA, which resulted in eutectic mixtures having severely depressed melting points relative to their components [129]. The highly decreased melting points were attributed to this peculiar structure, with the solvents also demonstrating good thermal and chemical stability, high viscosity, and low volatility [130]. In this regard, the DES can be an excellent medium to disrupt the inter-fibre structure of the lignocellulosic biomass matrix, which was a native material consisting mostly of cellulose, hemicellulose, and lignin. The destruction of these massive linkages was a needed and important process to enable the solubilization of sugars that can be used for energy production otherwise by fermentation. One of the most outstanding advantages of DES was its tunability. The combination and ratio of their constituent components can be changed and allowed DES to target specifically certain biomass structures.

The common DES combinations choline chloride as the HBA paired with a variety of HBDs, including urea, organic acids such as lactic acid, and polyols like glycerol. The resultant DES formulation may be optimized based on the type of processed biomass, such as agricultural residues, hardwoods, or grasses. DES broke the structure of lignin, exposed cellulose and hemicellulose and made them more accessible to enzymatic hydrolysis. The improved accessibility of these polymers resulted in higher yields of reducing sugars very important in producing biofuels and biochemicals. Many of the studies have highlighted that DES were not only saccharification enhancers but have other benefits in that they were recyclable and not energy-consuming compared to traditional methods [131].

ChCl with acetic acid has undertaken great success with rice straw, which was a residue generally high in hemicellulose. The lignin was reported to be selectively dissolved preventing condensation and polymerization, resulting in improved enzymatic hydrolysis and higher delignification of 83.1% and with 92.2% saccharification efficiency being reported [132]. Betaine hydrochloride can act as an alternative hydrogen bond acceptor and, likewise, has proven to be more potent in the degradation of more recalcitrant lignocellulosic biomass, for example, forest residues and agricultural stover. If, breaking lignin-cellulosic linkages of forest residues, it became very useful against more lignin-rich feedstocks. The combination of betaine together with glycerol, in this case, acted as an effective lignin reducer, whereby this reduction created an opportunity for more significant enzymatic access to cellulose; therefore, making the digestibility of biomass even more efficient. Ethanol yield reached 73.61%, which was a significant amount, given the recalcitrant nature thus usually associated with corn stover [133]. A DES mixture of betaine and lactic acid was particularly effective in delignification, lignin removal was reported to be 47.1% when applied to sugarcane bagasse [134]. A crop high biomass yield but relatively low in lignin content was miscanthus which responded well to the pretreatment using ChCl-glycerol DES formulation. The DES formulation not only preserved the integrity of cellulose but also showed some selectivity towards lignin, making it possible to achieve an ethanol yield of 72%v [89]. The preservation of the cellulose structure was equally important for an effective enzymatic hydrolysis to proceed. Another important, dedicated energy crop was switchgrass. ChCl-glycerol DES showed positive resulted in this material with a glucose yield of 89% thus the potential for the formulation of grass-like feedstocks was high [135]. DES based on glycerol were most promising in energy crops due to the balance between effective lignin solubilization and preservation of cellulose and hemicellulose components.

The primary research and development obstacles in the processing of LCB using deep eutectic solvent were high viscosity and low mass transfer efficiency, restricted lignin removal efficiency, possible carbohydrate degradation, and difficulty with solvent recovery and recyclability. Furthermore, DES-based processes scalability is still an issue. Researchers are creating low-viscosity and biodegradable DES, improving process conditions to remove lignin more effectively while maintaining fermentable sugars, and creating effective solvent recovery and recycling techniques in order to overcome these problems. In order to increase overall process efficiency and economic viability, integration with enzymatic hydrolysis and fermentation is also being investigated.

5-5. Wet oxidation

Wet oxidation pretreatment (WOT) pretreats LCB at high pressures and temperatures by combining air or oxygen with water [136]. This technique is called wet air oxidation when air is employed. WOT has been effectively used with various biomass sources and was carried out at temperatures between 150 and 320℃ [137] and air pressures

between 10 and 200 bar before heating [138]. This process had a major effect on the structure of lignin and yields more by-products [16], but less 5-hydroxymethylfurfural and furfural than steam explosion.

WOT has been combined with various CPT, like organic solvents, alkaline treatments, and steam explosion techniques to increase the total yield of fermentable sugars through subsequent enzymatic hydrolysis [139]. Pre-treatment efficiency was highly influenced by reaction temperature, reaction time, and oxygen pressure adjustments [12]. Equations (1) and (2) illustrate how the process used molecular O_2 in the aqueous phase to produce radicals that were essential to the process and to mineralise the substrates [138].

$$RH + O_2 \rightarrow R^* + HO_2^- \quad (1)$$

$$RH + HO_2^- \rightarrow R^* + H_2O_2 \quad (2)$$

Equations (3) and (4) illustrate how the produced radicals might combine with more O_2 and substrate to prolong the chain reaction.

$$R^* + O_2 \rightarrow ROO^* \quad (3)$$

$$R_1OO^* + R_2H \rightarrow R_1OOH + R_2^* \quad (4)$$

One of the most important steps in starting the depolymerisation of the components of LCB during the WOT of biomass was the creation of organic acids [12,138]. Solubilising most of the hemicelluloses and lignin made separating cellulose easier [137]. Acetyl groups de-esterification and the oxidation of hemicellulose fragments solubilise hemicelluloses to provide organic acids [140]. The degree of lignin removal was greatly influenced by the kind of LCB and the process parameters. Both oxidation and cleavage of lignin resulted in water-soluble carboxylic acids, including acetic, glutaric, succinic, oxalic, and formic acids. Some of these acids can even mineralised into carbon dioxide [12].

High energy requirements, the production of inhibitory chemicals, partial hemicellulose breakdown, and the demand for an effective oxygen supply were primary research and development issues in the wet oxidation pretreatment of LCB. Furthermore, scalability and reactor design continued to be issues for industrial applications. Researchers are investigating catalytic additives to improve lignin breakdown, refining reactor designs for greater scalability and energy efficiency, and optimising reaction conditions (like temperature, pressure, and oxygen levels) to minimise sugar degradation and inhibitor formation in order to address these problems. To improve overall biomass conversion, integration with downstream processes is also being investigated. The impact of different CPT for LCB is tabulated in Table 6.

6. Future Perspective

Enhancing biomass chemical pretreatment technologies and creating environmentally friendly chemical treatment innovations still have a lot of potential. Developing cost-effective and ecologically safe pretreatment techniques that facilitate total delignification and 100% conversion of biomass into bioproducts is essential. In order to create customised methods that consider the various compositions of LCB, future research should concentrate on fully comprehending the pretreatment reaction mechanisms. A thorough assessment of integrated or hybrid approaches, which combine two or more pretreatment techniques, is advised to attain higher levels of biomass deconstruction. Furthermore, low-cost, economically feasible biomass pretreatment techniques are required. For effective biomass refining, it is important to investigate the possibilities of LCB pretreatment using nanomaterials.

More investigation is needed to evaluate the suitability of different LCB types and the development of inhibitory agents. Future bioenergy production depends on evaluating environmentally friendly green solvents for pretreatment, including oxalic acid, succinic acid, acetic acid, fumaric acid, maleic acid, and citric acid. Subsequent investigations ought to concentrate on crafting ionic liquids with varied attributes to accommodate various LCB pretreatment techniques, diminishing the

Table 6. Summary of the effect of various chemical pretreatment methods

Biomass	Pretreatment method	Pretreatment parameters	Yield	Reference
Wheat straw	ILs	46.2 g of biomass	Ethanol (g/100 g substrate)	[50]
Sugar cane	DESs	84.2 g of biomass	Ethanol (g/100 g substrate)	[53]
Cotton stalks	Orgonsolv	21.5 g of biomass	Ethanol (g/100 g substrate)	[53]
Rice straw	Alkali	23.6 g of biomass	Ethanol (g/100 g substrate)	[54]
Sugar cane	ILs	23.9 g of biomass	Ethanol (g/100 g substrate)	[86]
Grass wate	Oxidative	55℃ for 6 h	83.5% enzymatic digestibility	[141]
Eucalyptus	DES	110℃ for 6 h	94% of glucose	[142]
Sugar cane bagasse	Orgonsolv	-	83% of delignification	[143]
Poplar	Ionic liquid	-	67% of delignification	[144]
Moso bamboo	DES	120℃ for 2 h	79.7% biomass conversion	[145]
Waste sawdust	Oxidative	-	287 mL/g of methane	[146]
Poplar	DES	100-160℃ for 3-9 h	90.8% of glucan	[147]
Wheat straw	Acid	160℃ for 30 min	0.586 g/g sugar	[148]
Sugar cane bagasse	Alkali	180℃ for 1 h	239 mL/g of Methane; 29.08 g of ethanol/100 g	[149]
Poplar	Oxidative	90℃ for 12 h	63% of delignification	[150]
Corn straw	Ionic liquid	150℃ for 3.5 h	68.3% of delignification	[151]
Corn stover	Acid	33.1 g of biomass	Ethanol (g/100 g substrate)	[152]

viscosity of ionic liquids, and augmenting the ionic liquid resistance of cellulase. To successfully commercialise and utilise emerging innovative methods for LCB pretreatment in biorefineries, it is imperative to evaluate their techno-economic viability. This calls for additional research into chemical pretreatment methods.

The goal of next-generation chemical pretreatment technologies for LCB is to reduce environmental impact while increasing cost-effectiveness, sustainability, and efficiency. These include the use of biodegradable deep eutectic solvents for the selective removal of lignin, catalytic oxidative pretreatment to improve the accessibility of cellulose, and low-cost organic acids as environmentally friendly substitutes for conventional acids. In order to increase sugar yields and enhance enzymatic hydrolysis, hybrid pretreatment strategies that combine chemical and biological techniques are also being investigated. Developments in lignin valorisation, recycling, and solvent recovery are essential to the economic viability of these next-generation technologies.

7. Conclusion

This article reviews the advancements in chemical pretreatment technology for the production of bioenergy from lignocellulosic biomass. An environmentally responsible and sustainable method that can support economic growth and energy security is the use of LCB-based biorefineries. By decreasing inhibitor production, improving delignification, and raising total bioenergy conversion efficiency, the ongoing developments in chemical pretreatment technology techniques have greatly enhanced biomass processing. It was determined that improved chemical pretreatment technology techniques, including acid, alkali, organosolv, deep eutectic solvent, ionic liquid, and wet oxidation, provide potential solutions for efficiently using lignocellulosic biomass for the generation of bioenergy. Every technique has its own advantages and disadvantages, but continuous research and development in enhancing solvent recovery, optimising reaction conditions, and combining pretreatment with fermentation and enzymatic hydrolysis is opening the door to more effective and profitable bioenergy production. In order to increase the production of biofuel and support the global shift to renewable energy sources, it will be essential to develop chemical pretreatment techniques that are both economical and environmentally friendly.

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References

1. Kumar, R., Kim, T. H., Basak, B., Patil, S. M., Kim, H. H., Ahn, Y., Yadav, K. K., Cabral-Pinto, M. M. and Jeon, B. H., "Emerging Approaches in Lignocellulosic Biomass Pretreatment and Anaerobic Bioprocesses for Sustainable Biofuels Production," *Journal of Cleaner Production*, **333**, 130180(2022).
2. Ufodike, C. O., Eze, V. O., Ahmed, M. F., Oluwalowo, A., Park, J. G., Liang, Z. and Wang, H., "Investigation of Molecular and Supramolecular Assemblies of Cellulose and Lignin of Lignocellulosic Materials by Spectroscopy and Thermal Analysis," *International Journal of Biological Macromolecules*, **146**, 916-921 (2020).
3. Rezania, S., Oryani, B., Cho, J., Talaiekhozani, A., Sabbagh, F., Hashemi, B., Rupani, P. F. and Mohammadi, A. A., "Different Pretreatment Technologies of Lignocellulosic Biomass for Bioethanol Production: An Overview," *Energy*, **199**, 117457(2020).
4. Abraham, A., Mathew, A. K., Park, H., Choi, O., Sindhu, R., Parameswaran, B., Pandey, A., Park, J. H. and Sang, B. I., "RETRACTED: Pretreatment Strategies for Enhanced Biogas Production from Lignocellulosic Biomass," *Bioresource Technology*, **301**, 122725(2020).
5. Rajamohan, S., Gopal, A. H., Muralidharan, K. R., Huang, Z., Paramasivam, B., Ayyasamy, T., Nguyen, X. P., Le, A. T. and Hoang, A. T., "Evaluation of Oxidation Stability and Engine Behaviors Operated by Prosopis Juliflora Biodiesel/diesel Fuel Blends with Presence of Synthetic Antioxidant," *Sustainable Energy Technologies and Assessments*, **52**, 102086(2022).
6. Gnansounou, E., Ganti, M. S., Singh, A. and Gabrielle, B., "Systems Analysis and Life-Cycle Assessment for Energy and Environmental Sustainability," *Bioresource Technology*, **317**, 123988(2020).
7. Zhou, Z., Liu, D. and Zhao, X., Conversion of Lignocellulose to Biofuels and Chemicals via Sugar Platform: An Updated Review on Chemistry and Mechanisms of Acid Hydrolysis of Lignocellulose," *Renewable and Sustainable Energy Reviews*, **146**, 111169 (2021).
8. Saini, J. K., Kaur, A. and Mathur, A., "Strategies to Enhance Enzymatic Hydrolysis of Lignocellulosic Biomass for Biorefinery Applications: a Review," *Bioresource Technology*, **360**, 127517 (2022).
9. Ahmed, N., Dhar, B. R., Pramanik, B. K., Forehead, H., Price, W. E. and Hai, F. I., "A Cookbook for Bioethanol From Macroalgae: Review of Selecting and Combining Processes to Enhance Bioethanol Production," *Current Pollution Reports*, 1-18(2021).

10. Mankar, A. R., Pandey, A., Modak, A. and Pant, K. K., "Pretreatment of Lignocellulosic Biomass: A Review on Recent Advances," *Bioresource Technology*, **334**, 125235(2021).
11. Shahbaz, M., Al-Ansari, T., Aslam, M., Khan, Z., Inayat, A., Athar, M., Naqvi, S. R., Ahmed, M. A. and McKay, G., "A State of the Art Review on Biomass Processing and Conversion Technologies to Produce Hydrogen and Its Recovery via Membrane Separation," *International Journal of Hydrogen Energy*, **45**(30), 15166-15195(2020).
12. Zhou, Z., Ouyang, D., Liu, D. and Zhao, X., "Oxidative Pretreatment of Lignocellulosic Biomass for Enzymatic Hydrolysis: Progress and Challenges," *Bioresource Technology*, **367**, 128208(2023).
13. Zhao, L., Sun, Z. F., Zhang, C. C., Nan, J., Ren, N. Q., Lee, D. J. and Chen, C., "Advances in Pretreatment of Lignocellulosic Biomass for Bioenergy Production: Challenges and Perspectives," *Bioresource Technology*, **343**, 126123(2022).
14. Chai, W. S., Bao, Y., Jin, P., Tang, G. and Zhou, L., "A Review on Ammonia, Ammonia-hydrogen and Ammonia-methane Fuels," *Renewable and Sustainable Energy Reviews*, **147**, 111254(2021).
15. Sankaran, R., Cruz, R. A. P., Pakalapati, H., Show, P. L., Ling, T. C., Chen, W. H. and Tao, Y., "Recent Advances in the Pretreatment of Microalgal and Lignocellulosic Biomass: a Comprehensive Review," *Bioresource Technology*, **298**, 122476(2020).
16. Beig, B., Riaz, M., Naqvi, S. R., Hassan, M., Zheng, Z., Karimi, K., Pugazhendhi, A., Atabani, A. E. and Chi, N. T. L., "Current Challenges and Innovative Developments in Pretreatment of Lignocellulosic Residues for Biofuel Production: A Review," *Fuel*, **287**, 119670(2021).
17. Hameed, Z., Naqvi, S. R., Naqvi, M., Ali, I., Taqvi, S. A. A., Gao, N., Hussain, S. A. and Hussain, S., "A Comprehensive Review on Thermal Coconversion of Biomass, Sludge, Coal, and Their Blends Using Thermogravimetric Analysis," *Journal of Chemistry*, **2020**(1), 5024369(2020).
18. Naqvi, S. R., Naqvi, M., Taqvi, S. A. A., Iqbal, F., Inayat, A., Khoja, A. H., Mehran, M. T., Ayoub, M., Shahbaz, M. and Amin, N. A. S., "Agro-industrial Residue Gasification Feasibility in Captive Power Plants: A South-Asian Case Study," *Energy*, **214**, 118952 (2021).
19. Chen, W. H., Lu, C. Y., Tran, K. Q., Lin, Y. L. and Naqvi, S. R., "A New Design of Catalytic Tube Reactor for Hydrogen Production from Ethanol Steam Reforming," *Fuel*, **281**, 118746(2020).
20. Ahmad, E., Khan, T. S., Alam, M. I., Pant, K. K. and Haider, M. A., "Understanding Reaction Kinetics, Deprotonation and Solvation of Brønsted Acidic Protons in Heteropolyacid Catalyzed Synthesis of Biorenewable Alkyl Levulinates," *Chemical Engineering Journal*, **400**, 125916(2020).
21. Bhatia, S. K., Jagtap, S. S., Bedekar, A. A., Bhatia, R. K., Patel, A. K., Pant, D., Banu, J. R., Rao, C. V., Kim, Y. G. and Yang, Y. H., "Recent Developments in Pretreatment Technologies on Lignocellulosic Biomass: Effect of Key Parameters, Technological Improvements, and Challenges," *Bioresource Technology*, **300**, 122724(2020).
22. Tayeh, H. N. A., Azaizeh, H. and Gerchman, Y., "Circular Economy in Olive Oil Production–olive Mill Solid Waste to Ethanol and Heavy Metal Sorbent Using Microwave Pretreatment," *Waste Management*, **113**, 321-328(2020).
23. Jamaldheen, S. B., Kurade, M. B., Basak, B., Yoo, C. G., Oh, K. K., Jeon, B. H. and Kim, T. H., "A Review on Physico-chemical Delignification as a Pretreatment of Lignocellulosic Biomass for Enhanced Bioconversion," *Bioresource Technology*, **346**, 126591 (2022).
24. Agrawal, R., Verma, A., Singhania, R. R., Varjani, S., Di Dong, C. and Patel, A. K., "Current Understanding of the Inhibition Factors and Their Mechanism of Action for the Lignocellulosic Biomass Hydrolysis," *Bioresource Technology*, **332**, 125042(2021).
25. Kumar, R., Kim, T. H., Basak, B., Patil, S. M., Kim, H. H., Ahn, Y., Yadav, K. K., Cabral-Pinto, M. M. and Jeon, B. H., "Emerging Approaches in Lignocellulosic Biomass Pretreatment and Anaerobic Bioprocesses for Sustainable Biofuels Production," *Journal of Cleaner Production*, **333**, 130180(2022).
26. Sai, B. A., Subramaniapillai, N., Mohamed, M. S. B. K. and Narayanan, A., "Optimization of Continuous Biodiesel Production from Rubber Seed Oil (RSO) Using Calcined Eggshells as Heterogeneous Catalyst," *Journal of Environmental Chemical Engineering*, **8**(1), 103603(2020).
27. Ganeshan, G., Shadangi, K. P. and Mohanty, K., "Degradation Kinetic Study of Pyrolysis and co-pyrolysis of Biomass with Polyethylene Terephthalate (PET) Using Coats–Redfern Method," *Journal of Thermal Analysis and Calorimetry*, **131**, 1803-1816 (2018).
28. Sai, B. A., Subramaniapillai, N., Mohamed, M. S. B. K. and Narayanan, A., "Optimization of Continuous Biodiesel Production from Rubber Seed Oil (RSO) Using Calcined Eggshells as Heterogeneous Catalyst," *Journal of Environmental Chemical Engineering*, **8**(1), 103603(2020).
29. Lim, H. Y., Tang, S. H., Chai, Y. H., Yusup, S. and Lim, M. T., "Co-pyrolysis of Plastics and Food Waste Mixture Under Flue Gas Condition for Bio-oil Production," *Sustainable Energy Technologies and Assessments*, **54**, 102826(2022).
30. Chen, L. Q., "Chemical Potential and Gibbs Free Energy," *Mrs Bulletin*, **44**(7), 520-523(2019).
31. Kumar, B., Bhardwaj, N., Agrawal, K., Chaturvedi, V. and Verma, P., "Current Perspective on Pretreatment Technologies Using Lignocellulosic Biomass: An Emerging Biorefinery Concept," *Fuel Processing Technology*, **199**, 106244(2020).
32. Sakthivel, R., Ramesh, K., Purnachandran, R. and Shameer, P. M., "A Review on the Properties, Performance and Emission Aspects of the Third Generation Biodiesels," *Renewable and Sustainable Energy Reviews*, **82**, 2970-2992(2018).
33. Zahrina, I., Yenti, S. R., Irianty, R. S. and Utama, P. S., "Catalytic co-pyrolysis of Palm Oil Empty Fruit Bunch and Waste Tire Using Calcium Oxide Catalysts for Upgrading Bio-oil," *Materials Today: Proceedings*, **87**, 321-326(2023).
34. Kaur, R., Gera, P., Jha, M. K. and Bhaskar, T., "Pyrolysis Kinetics and Thermodynamic Parameters of Castor (Ricinus communis) Residue Using Thermogravimetric Analysis," *Bioresource Technology*, **250**, 422-428(2018).
35. Ye, Y., Guo, W., Ngo, H. H., Wei, W., Cheng, D., Bui, X. T., Hoang, N. B. and Zhang, H., "Biofuel Production for Circular Bioeconomy: Present Scenario and Future Scope," *Science of The Total Environment*, **935**, 172863(2024).
36. Usmani, Z., Sharma, M., Gupta, P., Karpichev, Y., Gathergood, N., Bhat, R. and Gupta, V. K., "Ionic Liquid Based Pretreatment of Lignocellulosic Biomass for Enhanced Bioconversion," *Biore-*

source Technology, **304**, 123003(2020).
37. Monteiro, C. R., Avila, P. F., Pereira, M. A. F., Pereira, G. N., Bordignon, S. E., Zanella, E., Stambuk, B. U., de Oliveira, D., Goldbeck, R. and Poletto, P., "Hydrothermal Treatment on Depolymerization of Hemicellulose of Mango Seed Shell for the Production of Xylooligosaccharides," *Carbohydrate Polymers*, **253**, 117274 (2021).
38. Wang, C., Zhang, X., Liu, Q., Zhang, Q., Chen, L. and Ma, L., "A Review of Conversion of Lignocellulose Biomass to Liquid Transport Fuels by Integrated Refining Strategies," *Fuel Processing Technology*, **208**, 106485(2020).
39. Chen, S. and Davaritouchaee, M., "Nature-inspired Pretreatment of Lignocellulose–Perspective and Development," *Bioresource Technology*, **369**, 128456(2023).
40. Hu, J., Wang, Q., Wang, W., Xu, Z., Fu, J., Xu, Q., Wang, Z., Yuan, Z., Shen, F. and Qi, W., "Synthesis of a Stable Solid Acid Catalyst from Chloromethyl Polystyrene Through a Simple Sulfonation for Pretreatment of Lignocellulose in Aqueous Solution," *ChemSusChem*, **14**(3), 979-989(2021).
41. Ma, Y., Shen, Y. and Liu, Y., "State of the Art of Straw Treatment Technology: Challenges and Solutions Forward," *Bioresource Technology*, **313**, 123656(2020).
42. Pandey, A., Mankar, A. R., Ahmad, E. and Pant, K. K., "Deep Eutectic Solvents: A Greener Approach Towards Biorefineries," *In Biomass, Biofuels, Biochemicals*, 193-219(2021).
43. Si, M., Sillanpää, M., Zhuo, S., Zhang, J., Liu, M., Wang, S., Gao, C., Chai, L., Zhao, F. and Shi, Y., "Phase Separation of co-solvent Promotes Multiple Bio-nanomaterials Conversion from Natural Lignocellulose," *Industrial Crops and Products*, **152**, 112469(2020).
44. Chen, K., Sang, J., Wang, Z., Ibrahim, U. K., Xia, W., Guo, A., Zhang, J. and Hou, D., "Production of Low-oxygenated Bio-fuels (hydrocarbons and polymethylphenols) from Lignocellulose by a Two-stage Strategy with Non-noble Metal Catalysts," *Fuel*, **286**, 119401(2021).
45. Montoya-Rosales, J. J., Peces, M., González-Rodríguez, L. M., Alatriste-Mondragón, F. and Villa-Gómez, D. K., "A Broad Overview Comparing a Fungal, Thermal and Acid Pre-treatment of Bean Straw in Terms of Substrate and Anaerobic Digestion Effect," *Biomass and Bioenergy*, **142**, 105775(2020).
46. Toghiani, J., Malekzadeh, S., Jamali, N., Afsham, N., Fallah, N., Mahboubi, A., Nasernejad, B., Taherzadeh, M. J. and Oladzad, S., "Novel Advanced Oxidation Processes (AOPs) as Lignocellulosic Biomass Pretreatment Approaches and Their Sustainability Assessment: A Review," *Current Pollution Reports*, **10**(2), 207-246(2024).
47. Arora, A., Nandal, P., Singh, J. and Verma, M. L., "Nanobiotechnological Advancements in Lignocellulosic Biomass Pretreatment," *Materials Science for Energy Technologies*, **3**, 308-318(2020).
48. Quereshi, S., Ahmad, E., Pant, K. K. and Dutta, S., "Insights Into Microwave-assisted Synthesis of 5-ethoxymethylfurfural and Ethyl Levulinate Using Tungsten Disulfide as a Catalyst, *ACS Sustainable Chemistry & Engineering*, **8**(4), 1721-1729(2019).
49. Wang, Z., He, X., Yan, L., Wang, J., Hu, X., Sun, Q. and Zhang, H., Enhancing Enzymatic Hydrolysis of Corn Stover by Twin-screw Extrusion Pretreatment," *Industrial Crops and Products*, **143**, 111960(2020).
50. Ziaei-Rad, Z., Fooladi, J., Pazouki, M. and Gummadi, S. N., "Lignocellulosic Biomass Pre-treatment Using Low-cost Ionic Liquid for Bioethanol Production: An Economically Viable Method for Wheat Straw Fractionation," *Biomass and Bioenergy*, **151**, 106140(2021).
51. Bonfiglio, F., Cagno, M., Yamakawa, C. K. and Mussatto, S. I., "Production of Xylitol and Carotenoids from Switchgrass and Eucalyptus Globulus Hydrolysates Obtained by Intensified Steam Explosion Pretreatment," *Industrial Crops and Products*, **170**, 113800(2021).
52. Pan, S., Chi, Y., Zhou, L., Li, Z., Du, L. and Wei, Y., "Evaluation of Squeezing Pretreatment for Improving Methane Production from Fresh Banana Pseudo-stems," *Waste Management*, **102**, 900-908 (2020).
53. Liu, Y., Zheng, X., Tao, S., Hu, L., Zhang, X. and Lin, X., "Process Optimization for Deep Eutectic Solvent Pretreatment and Enzymatic Hydrolysis of Sugar Cane Bagasse for Cellulosic Ethanol Fermentation," *Renewable Energy*, **177**, 259-267(2021).
54. Wang, W., Tan, X., Imtiaz, M., Wang, Q., Miao, C., Yuan, Z., and Zhuang, X., "Rice Straw Pretreatment with KOH/urea for Enhancing Sugar Yield and Ethanol Production at Low Temperature," *Industrial Crops and Products*, **170**, 113776(2021).
55. Fonseca, B. G., Mateo, S., Roberto, I. C., Sánchez, S. and Moya, A. J., Bioconversion in Batch Bioreactor of Olive-tree Pruning Biomass Optimizing Treatments for Ethanol Production," *Biochemical Engineering Journal*, **164**, 107793(2020).
56. Ma, Y., Tan, W., Wang, J., Xu, J., Wang, K. and Jiang, J., "Liquefaction of Bamboo Biomass and Production of Three Fractions Containing Aromatic Compounds," *Journal of Bioresources and Bioproducts*, **5**(2), 114-123(2020).
57. Zhou, M. and Tian, X., "Development of Different Pretreatments and Related Technologies for Efficient Biomass Conversion of Lignocellulose," *International Journal of Biological Macromolecules*, **202**, 256-268(2022).
58. Meenakshisundaram, S., Fayeulle, A., Leonard, E., Ceballos, C. and Pauss, A., "Fiber Degradation and Carbohydrate Production by Combined Biological and Chemical/physicochemical Pretreatment Methods of Lignocellulosic Biomass–a Review," *Bioresource Technology*, **331**, 125053(2021).
59. Malik, K., Salama, E. S., Kim, T. H. and Li, X., "Enhanced Ethanol Production by Saccharomyces Cerevisiae Fermentation Post Acidic and Alkali Chemical Pretreatments of Cotton Stalk Lignocellulose," *International Biodeterioration & Biodegradation*, **147**, 104869(2020).
60. Haldar, D. and Purkait, M. K., "A Review on the Environment-friendly Emerging Techniques for Pretreatment of Lignocellulosic Biomass: Mechanistic Insight and Advancements," *Chemosphere*, **264**, 128523(2021).
61. Woiciechowski, A. L., Neto, C. J. D., de Souza Vandenberghe, L. P., de Carvalho Neto, D. P., Sydney, A. C. N., Letti, L. A. J., Karp, S. G., Torres, L. A. Z. and Soccol, C. R., "Lignocellulosic Biomass: Acid and Alkaline Pretreatments and Their Effects on Biomass Recalcitrance–Conventional Processing and Recent Advances," *Bioresource Technology*, **304**, 122848(2020).
62. Oka, D., Kobayashi, K., Isobe, N., Ogawa, Y., Yokoyama, T., Kimura, S., Kim, U. J., Tokuyasu, K. and Wada, M., "Enzymatic Hydrolysis of Wood with Alkaline Treatment," *Journal of Wood Science*, **59**, 484-488(2013).

63. Grimaldi, M. P., Marques, M. P., Laluce, C., Cilli, E. M. and Sponchiado, S. R. P., "Evaluation of Lime and Hydrothermal Pretreatments for Efficient Enzymatic Hydrolysis of Raw Sugarcane Bagasse," *Biotechnology for Biofuels*, **8**, 1-14(2015).
64. Kim, J. S., Lee, Y. Y. and Kim, T. H., "A Review on Alkaline Pretreatment Technology for Bioconversion of Lignocellulosic Biomass," *Bioresource Technology*, **199**, 42-48(2016).
65. Modenbach, A., "Sodium Hydroxide Pretreatment of Corn Stover and Subsequent Enzymatic Hydrolysis: An Investigation of Yields," Kinetic Modeling and Glucose Recovery(2013).
66. Yoon, L. W., Ang, T. N., Ngoh, G. C. and Chua, A. S. M., "Regression Analysis on Ionic Liquid Pretreatment of Sugarcane Bagasse and Assessment of Structural Changes," *Biomass and Bioenergy*, **36**, 160-169(2012).
67. Kim, I., Rehman, M. S. U. and Han, J. I., "Enhanced Glucose Yield and Structural Characterization of Corn Stover by Sodium Carbonate Pretreatment," *Bioresource Technology*, **152**, 316-320 (2014).
68. Zdeb, M., Skóra, A. and Pawłowska, M., "Influence of Temperature and Reaction Time on the Efficiency of Alkaline Pretreatment of Hay Biomass," *Journal of Ecological Engineering*, **22**(2), (2021).
69. Mafa, M. S., Malgas, S., Bhattacharya, A., Rashamuse, K. and Pletschke, B. I., "The Effects of Alkaline Pretreatment on Agricultural Biomasses (corn cob and sweet sorghum bagasse) and Their Hydrolysis by a Termite-derived Enzyme Cocktail," *Agronomy*, **10**(8), 1211(2020).
70. Tsai, M. H., Lee, W. C., Kuan, W. C., Sirisansaneeyakul, S. and Savarajara, A., "Evaluation of Different Pretreatments of Napier Grass for Enzymatic Saccharification and Ethanol Production," *Energy Science & Engineering*, **6**(6), 683-692(2018).
71. Dinabandhu Sahoo, D. S., Ummalyma, S. B., Okram, A. K., Sukumaran, R. K., George, E. and Ashok Pandey, A. P., "Potential of Brachiaria Mutica (Para grass) for Bioethanol Production from Loktak Lake," *Bioresource Technology*, **242**, 133-138(2017).
72. Awoyale, A. A., Lokhat, D. and Okete, P., "Investigation of the Effects of Pretreatment on the Elemental Composition of Ash Derived from Selected Nigerian Lignocellulosic Biomass," *Scientific Reports*, **11**(1), 21313(2021).
73. García-Negrón, V. and Toht, M. J., "Corn Stover Pretreatment with Na_2CO_3 Solution from Absorption of Recovered CO_2," *Fermentation*, **8**(11), 600(2022).
74. Mirmohamadsadeghi, S., Chen, Z. and Wan, C., "Reducing Biomass Recalcitrance via Mild Sodium Carbonate Pretreatment," *Bioresource Technology*, **209**, 386-390(2016).
75. Zhao, C., Shao, Q. and Chundawat, S. P., "Recent Advances on Ammonia-based Pretreatments of Lignocellulosic Biomass," *Bioresource Technology*, **298**, 122446(2020).
76. Ai, P., Zhang, X., Dinamarca, C., Elsayed, M., Yu, L., Xi, J. and Mei, Z., "Different Effects of Ozone and Aqueous Ammonia in a Combined Pretreatment Method on Rice Straw and Dairy Manure Fiber for Enhancing Biomethane Production," *Bioresource Technology*, **282**, 275-284(2019).
77. Shi, T., Lin, J., Li, J., Zhang, Y., Jiang, C., Lv, X., Fan, Z., Xiao, W., Xu, Y. and Liu, Z., "Pre-treatment of Sugarcane Bagasse with Aqueous Ammonia–glycerol Mixtures to Enhance Enzymatic Saccharification and Recovery of Ammonia," *Bioresource Technology*, **289**, 121628(2019).
78. Chen, Y., Cheng, J. J. and Creamer, K. S., "Inhibition of Anaerobic Digestion Process: A Review," *Bioresource Technology*, **99**(10), 4044-4064(2008).
79. Gu, Y., Zhang, Y. and Zhou, X., "Effect of Ca $(OH)_2$ Pretreatment on Extruded Rice Straw Anaerobic Digestion," *Bioresource Technology*, **196**, 116-122(2015).
80. Mustafa, A. M., Li, H., Radwan, A. A., Sheng, K. and Chen, X., "Effect of Hydrothermal and $Ca(OH)_2$ Pretreatments on Anaerobic Digestion of Sugarcane Bagasse for Biogas Production," *Bioresource Technology*, **259**, 54-60(2018).
81. Bharadwaj, A. S., Dev, S., Zhuang, J., Wang, Y., Yoo, C. G., Jeon, B. H., Aggarwal, S., Park, S. H. and Kim, T. H., "Review of Chemical Pretreatment of Lignocellulosic Biomass Using Low-liquid and Low-chemical Catalysts for Effective Bioconversion," *Bioresource Technology*, **368**, 128339(2023).
82. Cheah, W. Y., Sankaran, R., Show, P. L., Ibrahim, T., Baizura, T. N., Chew, K. W., Culaba, A. and Chang, J. S., "Pretreatment Methods for Lignocellulosic Biofuels Production: Current Advances, Challenges and Future Prospects," *Biofuel Research Journal*, **7**(1), 1115-1127(2020).
83. Alayoubi, R., Mehmood, N., Husson, E., Kouzayha, A., Tabcheh, M., Chaveriat, L., Sarazin, C. and Gosselin, I., "Low Temperature Ionic Liquid Pretreatment of Lignocellulosic Biomass to Enhance Bioethanol Yield," *Renewable Energy*, **145**, 1808-1816 (2020).
84. Roy, R., Rahman, M. S. and Raynie, D. E., "Recent Advances of Greener Pretreatment Technologies of Lignocellulose," *Current Research in Green and Sustainable Chemistry*, **3**, 100035(2020).
85. Zhang, J., Zhang, X., Yang, M., Singh, S. and Cheng, G., "Transforming Lignocellulosic Biomass Into Biofuels Enabled by Ionic Liquid Pretreatment," *Bioresource Technology*, **322**, 124522(2021).
86. Nakasu, P. Y. S., Ienczak, J. L., Rabelo, S. C. and Costa, A. C., "The Water Consumption of Sugarcane Bagasse Post-washing After Protic Ionic Liquid Pretreatment and Its Impact on 2G Ethanol Production," *Industrial Crops and Products*, **169**, 113642 (2021).
87. Nasirpour, N., Mohammadpourfard, M. and Heris, S. Z., "Ionic Liquids: Promising Compounds for Sustainable Chemical Processes and Applications," *Chemical Engineering Research and Design*, **160**, 264-300(2020).
88. Brandt, A., Gräsvik, J., Hallett, J. P. and Welton, T., "Deconstruction of Lignocellulosic Biomass with Ionic Liquids," *Green Chemistry*, **15**(3), 550-583(2013).
89. Hasanov, I., Raud, M. and Kikas, T., "The Role of Ionic Liquids in the Lignin Separation From Lignocellulosic Biomass," *Energies*, **13**(18), 4864(2020).
90. Rawat, S., Kumar, A. and Bhaskar, T., "Ionic Liquids for Separation of Lignin and Transformation Into Value-added Chemicals," *Current Opinion in Green and Sustainable Chemistry*, **34**, 100582(2022).
91. Qasim, U., Rafiq, S., Jamil, F., Ahmed, A., Ali, T., Kers, J., Khurram, M. S., Hussain, M., Inayat, A. and Park, Y. K., "Processing of Lignocellulose in Ionic Liquids: A Cleaner and Sustainable Approach, *Journal of Cleaner Production*, **323**, 129189(2021).
92. Taokaew, S. and Kriangkrai, W., Recent Progress in Processing Cellulose Using Ionic Liquids as Solvents," *Polysaccharides*, **3**(4), 671-691(2022).

93. Javed, K., Krumme, A., Krasnou, I., Mikli, V., Viirsalu, M., Plamus, T., Vassiljeva, V., Tarasova, E., Savest, N. and Mendez, J. D., "Impact of 1-butyl-3-methylimidazolium Chloride on the Electrospinning of Cellulose Acetate Nanofibers," *Journal of Macromolecular Science*, Part A, **55**(2), 142-147(2018).
94. Du, H. and Qian, X., "The Effects of Acetate Anion on Cellulose Dissolution and Reaction in Imidazolium Ionic Liquids," *Carbohydrate Research*, **346**(13), 1985-1990(2011).
95. Xie, W., Zhou, D., Ren, Y., Tang, S., Kuang, M. and Du, S. K., 1-Butyl-3-methylimidazolium Chloride Pretreatment of Cotton Stalk and Structure Characterization," *Renewable Energy*, **125**, 668-674(2018).
96. Amini, E., Valls, C. and Roncero, M. B., "Ionic Liquid-assisted Bioconversion of Lignocellulosic Biomass for the Development of Value-added Products," *Journal of Cleaner Production*, **326**, 129275(2021).
97. Moyer, P., Smith, M. D., Abdoulmoumine, N., Chmely, S. C., Smith, J. C., Petridis, L. and Labbé, N., "Relationship Between Lignocellulosic Biomass Dissolution and Physicochemical Properties of Ionic Liquids Composed of 3-methylimidazolium Cations And Carboxylate Anions," *Physical Chemistry Chemical Physics*, **20**(4), 2508-2516(2018).
98. Xin, B. and Hao, J., "Imidazolium-based Ionic Liquids Grafted on Solid Surfaces," *Chemical Society Reviews*, **43**(20), 7171-7187(2014).
99. Tanzin, T., Arabi, I. I., Mohinuddin, M. and Hossain, M. I., "Ammonium-based Ionic Liquids: Synthesis, Characterization, Computational Approach, Molecular Docking Study and Phytotoxicity Assessment," *Journal of Molecular Structure*, **1273**, 134337 (2023).
100. Sakthivel, S. and Velusamy, S., "Effect of Ammonium Based Ionic Liquids on the Rheological Behavior of the Heavy Crude Oil for High Pressure and High Temperature Conditions," *Petroleum*, **8**(4), 552-566(2022).
101. Blundell, R. K. and Licence, P., "Quaternary Ammonium and Phosphonium Based Ionic Liquids: a Comparison of Common Anions," *Physical Chemistry Chemical Physics*, **16**(29), 15278-15288(2014).
102. Mankar, A. R., Pandey, A., Modak, A. and Pant, K. K., "Pretreatment of Lignocellulosic Biomass: A Review on Recent Advances," *Bioresource Technology*, **334**, 125235(2021).
103. Bailey, J., Byrne, E.L., Goodrich, P., Kavanagh, P. and Swadźba-Kwaśny, M., "Protic Ionic Liquids for Sustainable Uses," *Green Chemistry*, **26**(3), 1092-1131(2024).
104. Mohammadi, M., Shafiei, M., Abdolmaleki, A., Karimi, K., Mikkola, J. P. and Larsson, C., "A Morpholinium Ionic Liquid for Rice Straw Pretreatment to Enhance Ethanol Production," *Industrial Crops and Products*, **139**, 111494(2019).
105. Sriariyanun, M., Kitiborwornkul, N., Tantayotai, P., Rattanaporn, K. and Show, P. L., "One-pot ionic Liquid-mediated Bioprocess for Pretreatment and Enzymatic Hydrolysis of Rice Straw with Ionic Liquid-tolerance Bacterial Cellulose," *Bioengineering*, **9**(1), 17(2022).
106. Srisampao, I., Pornwongthong, P., Roddecha, S., Rodiahwati, W. and Sriariyanun, M., Pretreatment Optimization of Cholinium Ionic Liquid for Maximizing Sugar Release From Rice Straw, In Proceedings of the 7th International Conference on Informatics, Environment, *Energy and Applications*, 169-173 (2018).
107. Wei, H. L., Wang, Y. T., Hong, Y. Y. and Zhu, M. J., "Pretreatment of Rice Straw with Recycled Ionic Liquids by Phase-separation Process for Low-cost Biorefinery," *Biotechnology and Applied Biochemistry*, **68**(4), 871-880(2021).
108. Poornejad, N., Karimi, K. and Behzad, T., "Ionic Liquid Pretreatment of Rice Straw to Enhance Saccharification and Bioethanol Production," *Journal of Biomass to Biofuel*, **1**, 8-15 (2014).
109. Jose, D., Raina, N., Deepakkumar, R., Panakkal, E. J., Sriariyanun, M. and Kangsadan, T., "The Combined Effect of Inorganic Salt and Ionic Liquid in Pretreatment on Enzymatic Saccharification of Rice Straw," In E3S Web of Conferences, *EDP Sciences*, **355**, 01002(2022).
110. Jose, D., Kitiborwornkul, N., Sriariyanun, M. and Keerthi, K., "A Review on Chemical Pretreatment Methods of Lignocellulosic Biomass: Recent Advances and Progress," *Applied Science and Engineering Progress*, **15**(4), 6210-6210(2022).
111. Poy, H., Lladosa, E., Gabaldón, C. and Loras, S., "Optimization of Rice Straw Pretreatment with 1-ethyl-3-methylimidazolium Acetate by the Response Surface Method," *Biomass Conversion and Biorefinery*, **13**(13), 12057-12072(2023).
112. Sun, J., Ding, R. and Yin, J., "Pretreatment of Corn Cobs and Corn Stalks with Tetrabutyl Phosphate Hydroxide Ionic Liquid to Enhance Enzymatic Hydrolysis Process," *Biochemical Engineering Journal*, **177**, 108270(2022).
113. Liu, Z., Li, L., Liu, C. and Xu, A., "Pretreatment of Corn Straw Using the Alkaline Solution of Ionic Liquids," *Bioresource Technology*, **260**, 417-420(2018).
114. Chen, J., Xu, Q., He, F., Yue, W., Hu, G., Gan, J. and Xie, H., "Pretreatment of Corn Stover by Levulinic Acid-based Protic Ionic Liquids for Enhanced Enzymatic Hydrolysis," *ACS Sustainable Chemistry & Engineering*, **10**(21), 7134-7148(2022).
115. Geng, X. and Henderson, W. A., "Pretreatment of Corn Stover by Combining Ionic Liquid Dissolution with Alkali Extraction," *Biotechnology and Bioengineering*, **109**(1), 84-91(2012).
116. Gao, D., Zhu, Q., Liu, P., Zhou, Q., Cheng, X., Liu, L., Xu, J. and Lu, X., "Efficient Pretreatment of Corn Straw with Ionic Liquid Composite System," *Journal of Inorganic and Organometallic Polymers and Materials*, **33**(7), 2000-2012(2023).
117. Ziaei-Rad, Z., Pazouki, M., Fooladi, J., Azin, M., Gummadi, S. N. and Allahverdi, A., "Investigation of a Robust Pretreatment Technique Based on Ultrasound-assisted, Cost-effective Ionic Liquid for Enhancing Saccharification and Bioethanol Production From Wheat Straw," *Scientific Reports*, **13**(1), 446(2023).
118. Ren, H., Zong, M. H., Wu, H. and Li, N., "Efficient Pretreatment of Wheat Straw Using Novel Renewable Cholinium Ionic Liquids to Improve Enzymatic Saccharification," *Industrial & Engineering Chemistry Research*, **55**(6), 1788-1795(2016).
119. Anuchi, S. O., Campbell, K. L. S. and Hallett, J. P., "Effective Pretreatment of Lignin-rich Coconut Wastes Using a Low-cost Ionic Liquid," *Scientific Reports*, **12**(1), 6108(2022).
120. da Silva, A. S. A., Lee, S. H., Endo, T. and Bon, E. P., "Major Improvement in the Rate and Yield of Enzymatic Saccharification of Sugarcane Bagasse via Pretreatment with the Ionic Liquid 1-ethyl-3-methylimidazolium Acetate ([Emim][Ac])," *Bioresource*

Technology, **102**(22), 10505-10509(2011).
121. Chambon, C. L., Mkhize, T. Y., Reddy, P., Brandt-Talbot, A., Deenadayalu, N., Fennell, P. S. and Hallett, J. P., "Pretreatment of South African Sugarcane Bagasse Using a Low-cost Protic Ionic Liquid: a Comparison of Whole, Depithed, Fibrous and Pith Bagasse Fractions," *Biotechnology for Biofuels*, **11**, 1-16(2018).
122. Pin, T. C., Nakasu, P. Y., Mattedi, S., Rabelo, S. C. and Costa, A. C., "Screening of Protic Ionic Liquids for Sugarcane Bagasse Pretreatment," *Fuel*, **235**, 1506-1514(2019).
123. Ziaei-Rad, Z. and Pazouki, M., "Cost-effective Ionic Liquid Pretreatment of Poplar Wood for Biofuel Production: An Optimization Study Using Response Surface Methodology," *Industrial Crops and Products*, **219**, 119036(2024).
124. Wang, Y., Kim, K. H., Jeong, K., Kim, N. K. and Yoo, C. G., "Sustainable Biorefinery Processes Using Renewable Deep Eutectic Solvents," *Current Opinion in Green and Sustainable Chemistry*, **27**, 100396(2021).
125. Tan, Y. T., Chua, A. S. M. and Ngoh, G. C., "Deep Eutectic Solvent for Lignocellulosic Biomass Fractionation and the Subsequent Conversion to Bio-based Products–A Review," *Bioresource Technology*, **297**, 122522(2020).
126. Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K. and Tambyrajah, V., "Novel Solvent Properties of Choline Chloride/urea Mixtures," *Chemical Communications*, (1), 70-71(2003).
127. Ma, C. Y., Gao, X., Peng, X. P., Gao, Y. F., Liu, J., Wen, J. L., and Yuan, T. Q., "Microwave-assisted Deep Eutectic Solvents (DES) Pretreatment of Control and Transgenic Poplars for Boosting the Lignin Valorization and Cellulose Bioconversion," *Industrial Crops and Products*, **164**, 113415(2021).
128. Flieger, J. and Flieger, M., "Ionic Liquids Toxicity—benefits and Threats," *International Journal of Molecular Sciences*, **21**(17), 6267(2020).
129. Ijardar, S. P., Singh, V. and Gardas, R. L., "Revisiting the Physicochemical Properties and Applications of Deep Eutectic Solvents," *Molecules*, **27**(4), 1368(2022).
130. Tan, Y. T., Chua, A. S. M. and Ngoh, G. C., "Deep Eutectic Solvent for Lignocellulosic Biomass Fractionation and the Subsequent Conversion to Bio-based Products–A Review," *Bioresource Technology*, **297**, 122522(2020).
131. Yan, G., Zhou, Y., Zhao, L., Wang, W., Yang, Y., Zhao, X., Chen, Y. and Yao, X., "Recycling of Deep Eutectic Solvent for Sustainable and Efficient Pretreatment of Corncob," *Industrial Crops and Products*, **183**, 115005(2022).
132. Maibam, P. D. and Goyal, A., "Approach to An Efficient Pretreatment Method for Rice Straw by Deep Eutectic Solvent for High Saccharification Efficiency," *Bioresource Technology*, **351**, 127057(2022).
133. Fu, X., Qiao, J., Xu, Z., Xu, C. and Li, X., "Deep Eutectic Solvent Cocktail Enhanced the Pretreatment Efficiency of Lignocellulose," *Industrial Crops and Products*, **210**, 118040(2024).
134. Chen, Y., Ma, C., Tang, W. and He, Y. C., "Comprehensive Understanding of Enzymatic Saccharification of Betaine: Lactic Acid-pretreated Sugarcane Bagasse," *Bioresource Technology*, **386**, 129485(2023).
135. Chen, Z., Reznicek, W. D. and Wan, C., "Deep Eutectic Solvent Pretreatment Enabling Full Utilization of Switchgrass," *Bioresource Technology*, **263**, 40-48(2018).
136. McGinnis, G. D., Wilson, W. W. and Mullen, C. E., "Biomass Pretreatment with Water and High-pressure Oxygen, The Wet-oxidation Process," *Industrial & Engineering Chemistry Product Research and Development*, **22**(2), 352-357(1983).
137. Castro, Y. A. and Agblevor, F. A., "Effect of Wet Air Oxidation on the Composition and Biomethanation of Water Hyacinth," *Biomass Conversion and Biorefinery*, **12**(7), 2737-2748(2022).
138. M'Arimi, M. M., Mecha, C. A., Kiprop, A. K. and Ramkat, R., "Recent Trends in Applications of Advanced Oxidation Processes (AOPs) in Bioenergy Production," *Renewable and Sustainable Energy Reviews*, **121**, 109669(2020).
139. Lee, J. T., Khan, M. U., Tian, H., Ee, A. W., Lim, E. Y., Dai, Y., Tong, Y. W. and Ahring, B. K., "Improving Methane Yield of Oil Palm Empty Fruit Bunches by Wet Oxidation Pretreatment: Mesophilic and Thermophilic Anaerobic Digestion Conditions and the Associated Global Warming Potential Effects," *Energy Conversion and Management*, **225**, 113438(2020).
140. Zhang, J., Zhou, H., Liu, D. and Zhao, X., "Pretreatment of Lignocellulosic Biomass for Efficient Enzymatic Saccharification of Cellulose. In Lignocellulosic Biomass to Liquid Biofuels," Academic Press, 17-65(2020).
141. Yan, X., Cheng, J. R., Wang, Y. T. and Zhu, M. J., "Enhanced Lignin Removal and Enzymolysis Efficiency of Grass Waste by Hydrogen Peroxide Synergized Dilute Alkali Pretreatment," *Bioresource Technology*, **301**, 122756(2020).
142. Shen, X. J., Wen, J. L., Mei, Q. Q., Chen, X., Sun, D., Yuan, T. Q. and Sun, R. C., "Facile Fractionation of Lignocelluloses by Biomass-derived Deep Eutectic Solvent (DES) Pretreatment for Cellulose Enzymatic Hydrolysis and Lignin Valorization," *Green Chemistry*, **21**(2), 275-283(2019).
143. Zhang, H., Zhang, J., Xie, J. and Qin, Y., "Effects of NaOH-catalyzed Organosolv Pretreatment and Surfactant on the Sugar Production from Sugarcane Bagasse," *Bioresource Technology*, **312**, 123601(2020).
144. Ho, M. C. and Wu, T. Y., "Sequential Pretreatment with Alkaline Hydrogen Peroxide and Choline Chloride: Copper (II) Chloride Dihydrate–synergistic Fractionation of Oil Palm Fronds," *Bioresource Technology*, **301**, 122684(2020).
145. Ling, Z., Guo, Z., Huang, C., Yao, L. and Xu, F., "Deconstruction of Oriented Crystalline Cellulose by Novel Levulinic Acid Based Deep Eutectic Solvents Pretreatment for Improved Enzymatic Accessibility," *Bioresource Technology*, **305**, 123025 (2020).
146. Almomani, F., Bhosale, R. R., Khraisheh, M. A. M. and Shawaqfah, M., "Enhancement of Biogas Production from Agricultural Wastes via Pre-treatment with Advanced Oxidation Processes," *Fuel*, **253**, 964-974(2019).
147. Wang, Y., Meng, X., Jeong, K., Li, S., Leem, G., Kim, K. H., Pu, Y., Ragauskas, A. J. and Yoo, C. G., "Investigation of a Lignin-based Deep Eutectic Solvent Using p-hydroxybenzoic Acid for Efficient Woody Biomass Conversion," *ACS Sustainable Chemistry & Engineering*, **8**(33), 12542-12553(2020).
148. Ruan, H., Fransen, S. C., Carter, A. H., Tao, H. and Yang, B., "Selecting Winter Wheat Straw for Cellulosic Ethanol Production in the Pacific Northwest, USA," *Biomass and Bioenergy*, **123**, 59-69(2019).
149. Nosratpour, M. J., Karimi, K. and Sadeghi, M., "Improvement

of Ethanol and Biogas Production from Sugarcane Bagasse Using Sodium Alkaline Pretreatments," *Journal of Environmental Management*, **226**, 329-339(2018).
150. Yuan, Z., Klinger, G. E., Nikafshar, S., Cui, Y., Fang, Z., Alherech, M., Goes, S., Anson, C., Singh, S. K., Bals, B. and Hodge, D. B., "Effective Biomass Fractionation Through Oxygen-enhanced Alkaline–oxidative Pretreatment," *ACS Sustainable Chemistry & Engineering*, **9**(3), 1118-1127(2021).
151. Pin, T. C., Nakasu, P. Y., Mattedi, S., Rabelo, S. C. and Costa, A. C., "Screening of Protic Ionic Liquids for Sugarcane Bagasse Pretreatment," *Fuel*, **235**, 1506-1514(2019).
152. Yu, J., Xu, Z., Liu, L., Chen, S., Wang, S. and Jin, M., "Process Integration for Ethanol Production from Corn and Corn Stover as Mixed Substrates," *Bioresource Technology*, **279**, 10-16(2019).

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