

A Review on Chemical Pretreatment Methods of Lignocellulosic Biomass: Recent Advances and Progress

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Abstract

The lignocellulose based biorefinery process plays a significant role in the production of value-added products to achieve the sustainable development goals that aim for a bio-circular-green economy. Due to the recalcitrant nature of the biomass components, different types of pretreatment methods are essential to make available carbohydrates for saccharification and fermentation. The mechanism, advantages, challenges, innovations, and technologies of various chemical pretreatment processes are summarized in this review. Based on the literature survey, chemicals such as acids, alkalis, organosolv, oxidative agents, ionic liquids, and deep eutectic solvents are covered in the review. Moreover, combined chemical pretreatment strategies are also discussed in this study, which can be utilized in industries. There are many challenges, such as the efficiency of the process, reaction conditions, formation of inhibitors, techno-economic feasibility, and environmental sustainability, which require further investigations to overcome these limitations to choose the best option for the feasible process. This review could be the guideline for the future direction in the improvement of pretreatment methods for the synthesis of value-added products.

Keywords: Biorefinery process, Chemical pretreatment methods, Deep eutectic solvent, Ionic liquids, Lignocellulosic biomass

1 Introduction

The sustainability of current economic strategies and utilization patterns is changed towards a Bio-Economy, Circular Economy, and Green Economy (BCG economy) that includes bio-based material, recycled products, and sustainable power [1], [2]. These strategies are adopted by both developed and developing countries due to rapid population growth, depletion of natural resources (e.g. fossil fuels), environmental pollution (e.g. Green gas emission), and climate change (Ozone layer depletion) [3]. The distribution of an exhaustive, and broad, guide

of targets and pointers supporting the 2030 Agenda for sustainable development goals (SDGs) in 2015 by the UN, gives a common outline to harmony and success for individuals and the planet, presently and into the future [4]. In this situation, the advancement of adaptable and coordinated biorefineries to produce biofuels and bioproducts from inexhaustible biomass sources address a critical approach to steer the change from an oil-based economy to a novel bioeconomy that searches for a more productive and sustainable global development [5]–[7]. Research, study, and execution related to biorefineries play an important role to assemble a solid bioeconomy structure in which

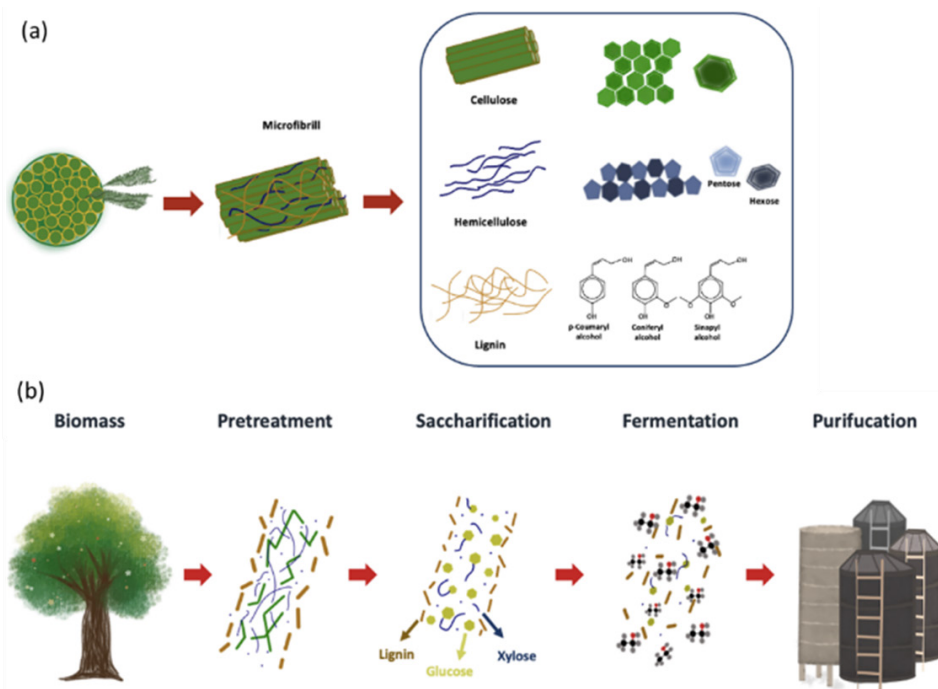


Figure 1: (a) Structure of lignocellulosic biomass before and after pretreatment. (b) Schematic representation of steps involved in the biorefinery process of lignocellulosic biomass.

biorefineries and sustainable production, and biomass sources can be profiled as promising choices for most SDGs [8]. Moreover, producing value-added products made the most encouraging pathway to accomplishing a resource effective BCG economy, which could be ranging from biofuels, biochemicals, and platform chemicals [2], [9]–[11]. Subsequently, it is an approach that focuses on safe, environmentally friendly chemical processes, minimizing waste discharges, producing new market potential openings, and utilizing resources more productively [12], [13]. In these circumstances, biomass plays a significant role to meet the SDGs goals.

In recent decades, Biomass is considered the largest renewable and sustainable energy source that can utilize and synthesize different energy forms and value-added products through the biorefinery process [14]. Among biomass, lignocellulosic biomass (LB) obtained from agricultural residues, energy crops, forest residues, and human waste is widely studied due to its huge scope accessibility, minimal expense, ability to produce energy, and eco-friendly products [15]. Lignocellulosic biomass is composed of cellulose,

hemicellulose, lignin, and other extracted substances in which the percentage of components varies in each plant species (Figure 1). Nevertheless, the complex and recalcitrant structure of lignocellulosic biomass is difficult for depolymerization of cellulose, solubilization of hemicellulose, removal of lignin, impeding the access of hydrolytic enzymes, and thus, lessening the effectiveness of the enzymatic hydrolysis [16]. To alter the recalcitrant nature of LB before converting it into a high-value product after the hydrolysis and fermentation process, various types of pretreatment methods are being examined and the challenges of pretreatment are revealed.

At present perspective, pretreatment methods are classified as biological, physical, chemical, and physicochemical types [17]. Furthermore, combined treatment strategies are demonstrated to increase the sugar yield and reduce the expense of production [18]. An effective pretreatment process should meet certain criteria, such as 1) enhancing the sugar yield, 2) avoiding the loss or degradation of polysaccharides, 3) preventing the formation of toxic byproducts that will inhibit the following saccharification and

fermentation processes, and 4) must be economical and profitable. Therefore, it is hard to mention, which pretreatment method is more suitable because it depends on the characteristics of the biomass and also the targeted end-product [19], [20]. However, the chemical pretreatment method is generally utilized in many industries as they are great for low lignin material. The overall aim of this review is to shed light on various chemical methods (acids, bases, oxidants, and solvents) used to convert LB into different value-added products. In addition, mechanisms, technologies, innovations, and challenges observed from the findings of researchers on different chemical method is reviewed in this paper.

2 Chemical Pretreatment Process

An important step involved in the biorefinery process is the pretreatment method (Figure 1). The main impediment that causes the large-scale production of biorefinery products from LB is the absence of an economically effective pretreatment method. The key information on each stage in the process concerning resulting market viability as well as methods is required for success in changing biomasses into sugars as building blocks for the development of value-added products [21]. Although, this step is the most expensive in the biorefinery process however it has incredible potential for upgrades in efficiency and bringing down expenses through further research and development.

As shown in Figure 1, cellulose is arranged as fibrils in the plant cell wall which contains 500–1400 glucose units that are bonded with $\beta(1-4)$ glycosidic bonds to form microfibrils. This microfibril with strong inter and intramolecular hydrogen bond provides a compact and rigid structure to cellulose. It exists in crystalline (ordered structure) and amorphous (disordered structure) states [22], [23]. Hemicellulose, which is amorphous in nature and composed of heteropolysaccharides (hexose and pentose sugars), coats the cellulose fibrils through weak interactions such as hydrogen bonds and Van der Waals force. Therefore, easy to remove when compared with cellulose due to its low strength [24], [25]. Another rigid structure that holds cellulose and hemicellulose is the lignin, which is composed of phenyl propane alcohol units (coumaryl, coniferyl, and sinapyl) with ether bonds. It contributes strongly to the recalcitrant

nature of LB [26]. The significant objective of the pretreatment process is to disrupt the structure of LB to cellulose, hemicellulose, and lignin to enhance the hydrolysis process and thus increase the yield of fermentable sugars.

Compared with the other pretreatment types, the chemical pretreatment method is considered very promising, since it can be quite effective in degrading more complex structured substrates [27], [28]. This method can be performed by applying various chemical processes of different natures. Chemical treatment is distinguished by the use of organic or inorganic compounds, which through interaction with the intra or interpolymer bonds of lignin, hemicellulose, and cellulose, lead to a disruption of the structure of LB [29]. Many approaches have been developed and have gained global attention because this method is economically effective with less utilization of energy as well as eco-friendly, faster reaction rates, and technology transfer availability that is more contrasted with physical and biological methods [2], [30]. In addition, this method improves the bioavailability of sugars by removing lignin and /or reducing the degree of polymerization and removing the crystalline structure of cellulose. This treatment method can delignify the cellulosic material and increase the level of biomass digestibility, therefore, it is widely used in the paper and pulp industry. It is also reported that some chemicals do not produce inhibitors in the downstream process and the reaction can be carried out at room temperature and pressure [27]. Chemicals including acids, alkalis, organosolv, oxidative agents, ionic liquids (ILs), and deep eutectic solvents (DES) are some of the common and widely researched chemical pretreatment methods used in the biorefinery industrial sector that are reviewed below sections (Figure 2). The mode of action, advantages, challenges, and innovations of different chemical methods are summarized in Table 1. Comparative analysis of different chemical pretreatment used to study various biomass was tabulated in Table 2.

3 Acid Pretreatment Methods

Acid pretreatment relies upon certain factors including different kinds of acids, their concentrations, solid to liquid proportion, and temperature. Acids include dilute to concentrated acids ranging from 0.2% to

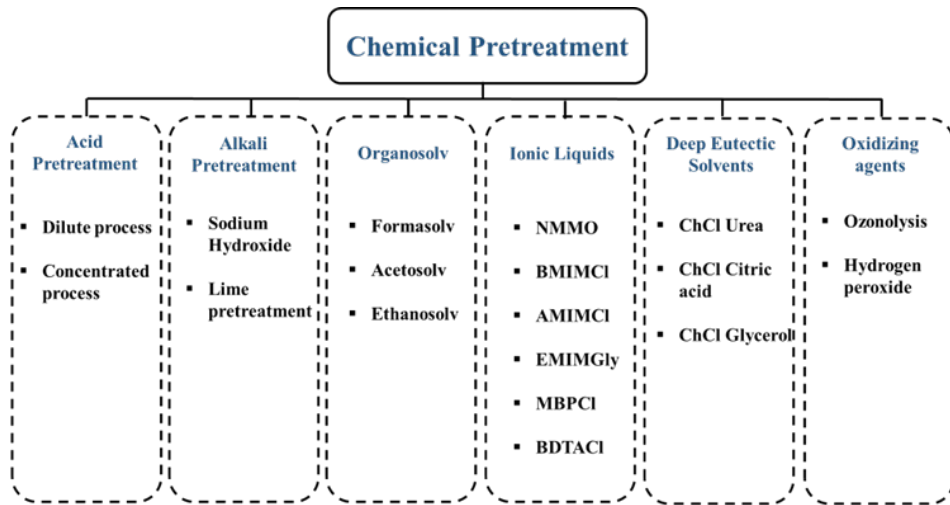


Figure 2: Different types of chemical pretreatment methods with examples.

Table 1: Mechanism, advantages, challenges, and advances in different chemical pretreatment methods

Pretreatment Method	Mode of Action	Advantages	Challenges	Innovations	References
Acid	Removes hemicellulose	High reaction rates of hemicellulose and high glucose yield	Corrosive effect, Require corrosive-resistant equipment, formation of inhibitors, and costly	Use of solid catalyst and the best operating condition to increase the efficiency of the process. High solid loading decreases the environmental effect. Regenerate the solid residue to make the process cost-effective	[29], [31]
Alkali	Removes lignin	Mild reaction conditions, an increase of enzymatic hydrolysis, and low formation of inhibitors	Unsuitable for woody biomass, long reaction time, and salt formation in the neutralization step	Applied for fractionation of LB	[32], [33]
Organosolv	Removes lignin	Obtain a pure form of value-added products, suitable for woody biomass, and easy recovery step	Require high operation conditions, high cost of organic solvents, and require safety measures to prevent environmental hazard formation	The use of organic solvents, such as methanol and ethanol can ease the recovery process, and fractionation of LB components can make the method economical.	[33], [34]
Oxidizing Agents	Removes lignin and slightly hemicellulose	Low reaction condition and absence of formation of inhibitors	Flammable, corrosive effect, an exothermic process required cooling systems, expensive oxidants, and a process	Oxidation performance can be increased by really directed in hydrated fixed bed reactor under atmospheric conditions.	[35], [36]
ILs	Removes lignin	Nonflammable, noncorrosive, recyclable, and eco-friendly	Expensive solvents, high solid loading, and inhibitory effects on hydrolysis enzymes	Protic ILs have less cost compared to dialkylimidazolium-based salts, the use of low-temperature condition help to reduce the degradation of both IL and biomass and allow recyclability	[27], [33]
DES	Removes lignin & hemicellulose	Less volatile, less toxic, eco-friendly, easy to handle, low cost and recyclable	High viscosity	Used for fractionation of varied biomass	[29], [19]

Table 2: Comparative analysis of various chemical pretreatment methods in various biomass

Biomass	Types of Chemical Pretreatment	Reaction Condition (Conc, Temp, Time, Solid Loading)	Hemicellulose (%)	Lignin (%)	Cellulose (%)	Sugar Yield (%)	Solid Recovery (%)	References
Rapeseed straw	Acid (Dilute phosphoric acid)	0.32% w/w, 180 °C, 30 min, 12% w/w	3.3	31.1	50	70.9	61	[37]
Corn cob	Acid (Carbon-based catalyst)	1% w/w, 140 °C, 360 min, 1% w/w	9.96	14.01	67.94	97.4	-	[38]
Banana Pseudostem	Acid (Conc. Sulphuric acid)	25% m/m, 121 °C, 30 min, 5 g	3.97	31.15	66.28	82	44.90	[39]
Elephant Grass (Leaf)	Acid (Conc. Sulphuric acid)	20% m/m, 121 °C, 30 min, 3 g	9.40	27.21	42.70	89.20	54.56	[40]
Banana Pseudostem	Alkali (Conc. Sodium hydroxide)	25% m/m, 121 °C, 30 min, 5 g	5.35	6.24	76.52	85	27.60	[39]
Pinewood (<i>Pinus eldarica</i>)	Alkali (Dilute Sodium hydroxide)	2% w/v, 180 °C, 300 min, 10 wt%	Negligible	23.9	70.2	83.5	54	[41]
Rice straw	Alkali (Lime)	8% w/v, 25 °C, 72 h, 5% w/v	20.2	11.7	38.1	66.8	-	[42]
Corn stover	Alkali (Ammonia)	4%w/v 35 °C, 5 days, 5 mm	24.81	5.88	34.67	80.6	-	[43]
Barley straw	Organosolv (acetosolv)	50:50 (acetone: water) & 35 mol/dm ³ H ₂ SO ₄ , 140 °C, 20 min, 100 g	7	19	50.8	75.4	48.5	[44]
Sweet sorghum stalk	Organosolv (ethanosolv)	50%v/v & 1% w/w H ₂ SO ₄ , 140 °C, 30 min, 25 g	15	12.4	38.7	77	-	[45]
Sugarcane bagasse	Organosolv (formasolv)	78 wt% & 0.1 wt% H ₂ SO ₄ , 107 °C, 90 min, 30g	6.3	15.7	81.1	86.9	48.2	[46]
Sugarcane bagasse	Oxidizing agent (Ozonolysis)	3.44% v/v, 40% w/w moisture content, 120 min, 35 g	98.7	13.7	92.5	46	-	[47]
Banana Pseudostem	Oxidizing agent (Hydrogen peroxide)	4% m/m, 25 °C, 240 min, 5 g	14.17	10.49	66.91	74	42.70	[39]
Mixed softwood (<i>Pinus rigida</i> and <i>Pinus densiflora</i>)	ILs (1-butyl-3-methylimidazolium acetate)	1:20 w/w 100 °C, 15 h, 0.2 g	15.3	30.2	43.7	92.5	92.5	[48]
Oil palm frond	ILs (1-ethyl-3-methylimidazolium diethyl phosphate)	1:10 w/w, 90 °C, 240 min, 0.25 to 0.5 mm	12.1	8.5	68.5	-	-	[49]
Corn cob	DES (ChCl:ethylene glycol)	1:2, 6 g solvent, 90 °C, 24 h, 0.3 g	-	87.6	-	85.3	73.4	[50]
Potato peels	DES (ChCl:glycerol)	1:2, 115 °C, 3 h, 1:16 (biomass to solvent ratio)	3.3	27.2	44	41.9	75	[51]
Switchgrass	DES (Aqueous ChCl:glycerol)	1:2, 15 g solvent, 20 wt% water, 121 °C, 1 h, 1.5 g	7.36	14.89	60.32	88.9	49.41	[52]
Rice straw	DES (ChCl formic acid:acetic acid:foraceline)	1:1:1, 200 g solvent, 130 °C, 120 min, 10 g	3.1	27.2	50.8	-	-	[53]

2.5% w/w to the biomass, and are continually stirred at low to high temperatures (30 °C to 210 °C), respectively [37]. Using the acid pretreatment method, the hemicellulose structure gets hydrolyzed but the cellulose and lignin structure stayed less impacted [54]. A high concentration of acid in the pretreatment will cause cellulose to convert to sugars. Moreover, in severe conditions sugars are converted to many by-products (e.g. furfural, Hydroxymethylfurfural, levulinic acid, methyl furfural, etc.) [19], [55], [56]. The method is appropriate for biomass with low lignin content since the lignin is not degraded from the raw material. Besides, the optimal reaction condition of the acid pretreatment is extremely important [54].

Dilute acid pretreatment has gained wide consideration from many studies because of its benefits, for instance, increased level of cellulose in the pretreated substrate, requiring fewer prerequisite enzymes, and generating low inhibitors. Dilute acids ranging from 0.1% to 2% (w/v) are conducted in two different conditions. One at high temperature (more than 160 °C) in continuous mode for low solid loading (5 to 10 wt%) and another at low temperature (less than 160 °C) in batch mode with increased solid loading (10 to 40 wt%) reactions are generally used in the dilute acid pretreatment method [36]. The main application of this method is utilized for the production of bioethanol and biogas. One of the advantages is the use of inorganic or mineral acids (Sulfuric, Hydrochloric, Phosphoric, and Nitric acids) and organic acids (Maleic, Fumaric, and Oxalic acids), which are highly commercialized compounds that can be utilized for the scale-up to an industrial level. However, other choices were investigated recently by utilizing solid catalysts (e.g. zeolites, ion-exchange resins, and carbon-based catalysts) [31]. The drawback of using an excessive catalytic load is that it adversely affects the pretreatment process, resulting in low glucose yields as a result of the formation of adequate acid sites, which accelerates unwanted side reactions. Nevertheless, the most significant benefit of using a solid acid catalyst is its recyclability [57], [38].

In the concentrated acid treatment method, all acids are taken in high concentration (more than 20% v/v) at below 100 °C temperature for the reaction to obtain high oligomers or monosaccharides avoiding the hydrolysis step using enzymes [58]. This process is categorized into three steps; 1) degradation of

hemicellulose, 2) impact on cellulose to obtain carbohydrates, and 3) monosaccharides produced after saccharification. Concentrated acid pretreatment (sulfuric acid and phosphoric acid) showed a potentially high yield of sugar when compared with dilute acid pretreatment [39], [40]. Despite the aforementioned advantages, concentrated acid pretreatment causes disadvantages, such as acid corrosion, and the formation of highly toxic substances that will inhibit the hydrolysis and fermentation steps. Furthermore, additional costs were required for the downstream process for acid recovery and purification of the end-product.

4 Alkali Pretreatment Methods

The use of alkali in the pretreatment method leads the lignocellulosic material to break the ester and glycosidic bond, which allows the degradation of the lignin and affects the recalcitrant nature of the cellulosic structure [59], [29]. The bases, such as sodium, potassium, calcium, and ammonia are mostly utilized in the pretreatment of LB under low temperature and pressure. The solid fraction obtained after pretreatment contains cellulose and the liquid fraction contains hemicelluloses, lignin, and other inorganic chemicals. Like, acid pretreatment, concentration, solid liquid ratio, and optimum conditions (temperature, pressure, and time) are the factors that led to the efficiency of the alkali pretreatment method [32], [30]. The concentration of alkali below 4% is usually used at high temperature and pressure, which results in less corrosion effect, formation of inhibitors, and sugar degradation than acid pretreatment. The demerit of this method is that it takes a long reaction time and hard to neutralize the posttreatment fraction [33].

Among alkalis, sodium hydroxide (NaOH) gained the attention of researchers for the pretreatment of various biomass including crop straws, bamboo, and banana pseudostem for the production of biogas, bioethanol, and glucose respectively, due to its potential in delignification and reducing the crystallinity of cellulose [60], [61], [39]. It removes acetyl and other uronic acid substitutions from hemicelluloses, which potentially increases the availability of enzymes in the cellulose structure [62]. Ali et al studied the effect of dilute alkali pretreatment at a low concentration of NaOH (2%w/v) at 180 °C and obtained 78.0% of ethanol and high biogas yield of 244 mL/g at 1% w/v

NaOH of the same temperature (180 °C) from softwood pine [41]. Increasing NaOH concentration to 25% resulted in a high yield of glucose as a result of the removal of lignin and hemicellulose [39]. Moreover, it affects microbial growth during fermentation and is strenuous to recycle [63]. To rectify the soil salinization caused by NaOH, other chemical reagents are used, such as potassium hydroxide (KOH) and calcium oxide (CaO). However, CaO is less efficient than NaOH and KOH are more expensive than NaOH [64], [65].

Another alkaline pretreatment that is most commonly used is the Lime treatment using calcium hydroxide (CaOH) [42]. The mechanism that happens after lime treatment is the release of acetyl groups from hemicelluloses, which lowers the enzyme barrier and increases the cellulose depolymerization. This method can treat the biomass under different conditions, such as high or low temperature for short or long pretreatment duration, absence or presence of air or oxygen. Moreover, it has advantages over NaOH, for instance, low cost, simple technique, and efficient delignification [66]. Ammonia is the other alkaline pretreatment used for the anaerobic digestion process of corn stover for biogas production with the same mechanism [43], [67]. However, salt formation during the neutralization process is the main challenge in the alkaline pretreatment method. Additionally, a few types of research have been done by taking advantage of acid and alkaline pretreatments to develop sequential acid/alkali pretreatment and the diluted chemicals were applied with high sugar yield recovery [68].

5 Organosolv Methods

To extract pure lignin from LB, the organosolv method is used, in which an organic solvent (methanol, ethanol, acetone, acetic acid peracetic acid, etc.) mixture is utilized in the presence or absence of a catalyst (acid, base, or salt) [69]. During the reaction, there is the breakage of the intrinsic chemical bond between lignin and hemicellulose, thus obtaining the pure form of lignin, hemicellulose, polysaccharides, and almost pure cellulose [32]. The variation of the organosolv method is based on reaction conditions, such as temperature, pressure, reaction time, type of solvent, and catalyst used.

According to the study by Zhang *et al.*, the presence of a catalyst in the reaction can enhance the purity of

the derived products that occur at low temperatures and short retention duration [34]. Acetone (acetosolv) with acid catalyst (H_2SO_4) achieved a high yield of cellulose (75.4%) where the concentration of H_2SO_4 impacts both biomass fractionation and saccharification yield significantly [44]. Ethanol (ethanosolv) is a promising solvent to utilize for biogas production because it is highly effective on wheat straw and simply recovered the substrate through a distillation process [70], [45]. In addition, it is cost-effective and less toxic to humans than other solvents, for instance, methanol [71]. Among acid catalysts, formic acid (formasolv) is relevantly used as it has a high lignin dissolution under low temperature and pressure resulting in the formylation of biomass that causes an increase in cellulose digestibility [46]. Moreover, low corrosive effects and the formation of hazards are observed when compared with other mineral acids, such as sulphuric acid and hydrochloric acid [72]. As the organic solvent has less boiling point, it has an effect on volatility and also risks the operation at high pressure, which causes the major disadvantage of the organosolv pretreatment method [30].

6 Oxidizing Agents

The application of oxidative methods, such as ozonolysis and hydrogen peroxide helps the delignification process during the pretreatment of biomass. Oxidizing agents react with the aromatic ring of lignin resulting in the formation of carboxylic acid that acts as an inhibitor in the growth of microorganisms, however, it can be removed by washing step [36], [32]. Likewise, in other aforementioned methods, the conversion of biomass components is affected based on the type of raw material, the concentration of oxygen, and reaction conditions [35].

Ozone in the ozonolysis method performed under atmospheric conditions is one of the strong oxidizing agents that is stable at low pH. This method explicitly attacks both the side chain and phenolic structure of lignin, thus resulting in less loss of hemicellulose and cellulose [47]. Therefore, the rate of enzymatic hydrolysis is increased due to the delignification of LB [54]. Another oxidizing agent having a similar mechanism is hydrogen peroxide. The banana pseudostem is pretreated with hydrogen peroxide and a high sugar yield obtained is 74% when treated at 4%

w/w concentration [39]. Other oxidizing agents include peracetic acid, sulfur trioxide, and chlorine dioxide degrade lignin as well as hemicellulose at alkaline or neutral pH. However, expensive oxidants and corrosive effects are the obstacles faced while using them in the industrial sector [33].

7 Ionic Liquids (ILs)

The ionic liquid is considered to be a green solvent for various applications. ILs have many advantages over other chemicals that include, eco-friendly, recyclability, less corrosive, less volatile, less viscosity, chemical inertness, better thermal stability, nonflammable, and high polarity [73]. They mostly appear as liquid state salts at room temperature [74]. This chemical is highly effective for the valorization of various biomass due to its ability to degrade lignin and dissolve cellulose [75].

ILs are composed of inorganic anions (halogens, formates, acetates, amides, imides, thiocyanates, phosphates, sulfates, sulfonates, and dichloroaluminates) and organic cations (imidazolium, phosphonium, pyrrolidinium, and cholinium), which their properties can be altered based on their chemical composition and preparation strategy [50], [76]. In addition, they work differently in the dissolution of LB with the maximum recovery yield of carbohydrates after fermentation at optimum conditions [48]. Therefore, a large number of combinations are made and studied by many researchers based on various purposes, especially for the depolymerization of cellulose to increase the efficiency of the pretreatment process [19]. Room temperature ionic liquids (RTILs) are of special interest salts that exist in a liquid state at room temperature and can be usable at low temperatures (below 100 °C) [77].

Recovery of ILs from carbohydrates and other components from the reaction mixture after the pretreatment process is one of the strenuous steps required in this method [72]. The study of Financie et al showed an efficient removal of lignin together with IL pretreatment using 1-ethyl-3-methylimidazolium diethyl phosphate followed by enzymatic delignification of oil palm front biomass and recovered 90% of IL after the recycling process [49]. Zou et al investigated many recovery processes and came to the conclusion that distillation is the efficient process to recover ILs [78]. Nevertheless, the cost and energy requirements are high, which causes challenges to produce the pilot

scale in biorefineries.

Although the high efficiency of IL pretreatment has been demonstrated as discussed in this work, the limitations of this method have been described for various aspects, for example, high cost of IL, inhibition of IL residue to cellulose activities, and toxicity to microbial activities used in fermentation step [79]–[81]. Therefore, many attempts to develop IL pretreatments have been conducted with various state-of-art strategies. For example, low concentrations of two ILs, pyridinium hydrogen sulfate (PyH)(H₂SO₄) and triethylammonium hydrogen sulfate (TEA)(H₂SO₄), were applied to pretreat coconut waste with an optimization technique and showed success to obtain the similar yield to concentrated IL [82]. To reduce the cost of IL, recycling and reuse processes in various lignocellulose pretreatment have been conveyed and 5 times IL recycling was demonstrated [83], [84]. In the case of toxicity of IL residue to cellulase activities and microbial viability, IL types with less toxic and IL-tolerant cellulases were applied to the process to compromise the inhibitory effects of IL residues [80], [85].

8 Deep Eutectic Solvents

A recent development in the chemical pretreatment process is the utilization of deep eutectic solvent (DES), which popularity started in 2015 onwards [2]. Comparatively, DESs are low costs and easy to prepare than ILs [86]. DES is also considered a green solvent like ILs. Similarly, it is used for delignification in the absence of condensation reaction [87]. DES is prepared by combining two or more constituent mixtures containing hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) [88]. According to the study by Chen & Mu, DES efficiently allows the dissolution of biomass components and increases the recovery yield of carbohydrates as it allows the breakage of the strong intermolecular hydrogen bond [89]. The lignin obtained has significant properties, such as being highly potent for the valorization of the product, high purity, less molecular weight, and, surprisingly, a higher substance of uncondensed structures and phenolic groups [87].

Many mixtures can be utilized for the synthesis of DESs, allowing the tailor-made design of DES mixtures. Choline DES is mostly studied, which is a type of solvent formed by a covalent and hydrogen

bond between the choline anion and coordination agent [90]. This helps cellulose moderately stable and exhibit high solubility toward lignin [91]. The synthesis of choline chloride (ChCl) with basic acid (mono, di & poly), commonly used HBA, potentially removes hemicellulose and lignin resulting in 90% cellulose digestibility from the biomass corncob and food wastes [92], [51]. Different types of ChCl DES include ChCl urea, ChCl citric acid, ChCl glycerol, and ChCl oxalic acid. Depending upon the nature of HBD (more acidic or alkaline), variation in sugar recovery yield (high) occurs. In contrast, neutral HBD (e.g. ChCl glycerol) combined with water results in 88.9% glucose yield [52]. Several novel classes of DES, for instance, dihydrogen bonding DES (formic acid and acetic acid) showed effectual delignification, and cellulose digestibility when treated with rice straw [53]. However, more research studies were needed to understand the mechanism of DES in order to improve the efficiency of the process.

DES pretreatment can be combined with other pretreatment methods to improve the process efficiency. Recently, DES pretreatments using choline chloride (ChCl) with urea (U), glycerol (G), and lactic acid (LA) were combined with hydrothermal pretreatment and applied for pretreatment of rice straw, napier grass, and sugarcane bagasse [93]. Interestingly, when all these three biomasses were mixed together, the DES pretreatment efficiency was not compromised and had a similar range of sugar yields as obtained from single types of biomass [94]. This study suggested the flexibility of DES chemicals to various types of lignocellulose, which could be a solution for industrial application in the future.

9 Combined Chemical Pretreatment Methods

To overcome the limitations of chemical pretreatment methods listed in Table 1, some studies have been conducted by the researchers on a combination of pretreatment methods with the use of low energy and high usage of biomass constituents for pretreatment in order to increase the efficiency of the process, obtaining high yield of sugar and lowers the cost of operation [18], [95], [96]. In this section, a few consolidated pretreatments involved in the chemical method are discussed, and sugar yields after the single and combined pretreatment method of some studies are

mentioned in Table 3.

The acid and alkali multi-step pretreatment methods are promising approaches, which can rectify the neutralization process and lowers or removes the formation of inhibitors [97]. The yield of sugar can be increased when compared with single-step pretreatment due to an increase in the porosity and degradation of hemicellulose and lignin structure to aid effective enzymatic saccharification after acid and alkali pretreatment of the biomass in a multi-step process [98]. In alkaline and hydrogen peroxide combination, the formation of hydroxyl radicals and superoxides occurs due to the instability of hydrogen peroxide in alkaline conditions that cause the variation in the rate of delignification of LB depending on the reaction conditions [99], [100]. Munoz *et al.* investigated the combination pretreatment (sodium hydroxide and hydrogen peroxide) in corn straw and removed a high rate of lignin and hemicellulose are 93% and 83%, respectively [101].

Olavo *et al.* conducted a combination study using unpressurized ozonolysis and acid (dilute sulfuric acid) on sugarcane bagasse to increase the yield of cellulosic ethanol (threefold) in the absence of high pressure and temperature. This study showed a high yield of glucan and xylan compared with the single pretreatment method. Ozonolysis combined with alkali (sodium hydroxide) showed 10% removal of lignin and high sugar recovery compared with alkali alone pretreatment [16]. This is due to the high degradation of cellulose occurring during oxidation [102]. The combination of organic solvent (aqueous ethanol) with acetic acid and alkaline hydrogen peroxide increases the saccharification rate because the combined pretreatment affects the depolymerization of LB components and helps to increase the enzyme accessibility to the substrate [103].

Another combination approach is with ionic liquids and acid pretreatment, which increases the efficiency of the hydrolytic enzymes with a high rate of sugars [104]. The study of pretreatment combination with ionic liquid with alkali (ammonia) acted on the cell wall of biomass (Eucalyptus) causes the change in the morphological structure of LB [105]. Moreover, Lu *et al.* featured the significance of anions over the cations in the consolidated pretreatment process. Thus, the consolidated pretreatment alongside other pretreatments can assist with promoting improve the expected yield from different biomasses. [106]. Furthermore, the

Table 3: Efficiency of the process on different biomass using different DES

Biomass	Pretreatment Method	Conditions (Conc., Temp, Time, solid loading)	Yield after Single Pretreatment		Yield after Combined Pretreatment		References
			Glucose (%)	Xylose (%)	Glucose (%)	Xylose (%)	
Corn stover	Alkali-acid	<ul style="list-style-type: none"> 2% (w/w) NaOH, 121 °C, 20 min, 10% (w/w) 1% (w/w) H₂SO₄, 160 °C, 10 min, 10% (w/w) 	<ul style="list-style-type: none"> 28.19 31.22 	<ul style="list-style-type: none"> 13.59 16.76 	30.58	17.12	[97]
Sugarcane bagasse	Acid-Alkali	<ul style="list-style-type: none"> 1% (w/v) H₂SO₄, 121 °C, 30 min, 27% (w/w) 3% (w/v) NaOH, 100 °C, 40 min, 27% (w/w) 	<ul style="list-style-type: none"> 35.6 60.4 	<ul style="list-style-type: none"> 26.4 16.8 	80.9	Not reported	[98]
Sweet sorghum bagasse	Dilute alkaline-Hydrogen peroxide	<ul style="list-style-type: none"> 100 mL 2% (w/v) NaOH, 121 °C, 60 min, 10 g 5% (w/v) H₂O₂, room temp., 24 h, 10 g 	<ul style="list-style-type: none"> 82.08 72.45 	<ul style="list-style-type: none"> 9.45 17.52 	74.29	Not reported	[100]
Sugarcane bagasse	Ozonolysis- acid	<ul style="list-style-type: none"> 50% (w/v) of biomass with water, 60 min under a gas flow of 32 mg O₃ min⁻¹ 0.1 Mol L⁻¹ H₂SO₄, 25 °C, 2 h, 5% (w/v) 	<ul style="list-style-type: none"> 45 33 	<ul style="list-style-type: none"> 65 57 	76	83	[16]
Sugarcane bagasse	Ozonolysis-alkaline	<ul style="list-style-type: none"> 15:1, 0.5 MPa O₂, 80 °C, 120 min, 4 g 1% (w/v) NaOH, 80 °C, 120 min, 4 g 	NaOH: 77.51	64.93	93.03	83.98	[102]
Tea oil fruit hull	Organosolv-alkaline hydrogen peroxide (AHP)	<ul style="list-style-type: none"> Acetic acid organosolv (AAO): 53% (v/v), 0.6% (w/v) H₂SO₄, 125 °C, 1.72 h, 10.5 g AHP:3% (v/v) H₂O₂, pH 11.5 using NaOH, room temp., 12 h, 12.5% (w/w) 	AAO alone: 50	Not reported	85	Not reported	[103]
Sunflower stalk	ILs-acid	<ul style="list-style-type: none"> 25%, (w/w) 1-butyl-3-methyl imidazolium Chloride, 90 °C, 2 h 0.5% w/v NaOH, 50 mM, pH 5.0 acetate buffer, 90 °C, 2 h, 5% (w/w) 	<ul style="list-style-type: none"> 7.96 9.738 	Not reported	16.342	Not reported	[104]
Eucalyptus	ILs- Alkali	<ul style="list-style-type: none"> 5% (wt) 1-butyl-3-methylimidazolium acetate, 120 °C, 30 min, 5 g 4% NaOH, 90 °C, 2 h 	IL: 62.6	Not reported	90.53	Not reported	[105]

fractionation process of lignocellulose, for example, wax extraction combined with alkaline pretreatment, was demonstrated to enhance the sugar yield recovery from the lignocellulose. Also, the wax by-products were estimated to gain the revenue of the overall ethanol production process by 1.6–2.4 times [107], [108]. All of the combination methods and above discussed yield high sugar recovery, dissolution, and removal of LB components (lignin, hemicelluloses,

and cellulose) from raw material than single-step pretreatment is shown in Table 3. Moreover, it allows for the better fractionation of biomass. However, these combined processes require further investigation of pretreatment conditions (raw material, reaction time, energy, and operation cost), to stay away from extra complexities in processing and economic analysis to make them viable in the scale up of value-added products commercially

10 Techniques Used to Study Pretreatment Efficiency

As aforementioned, after the pretreatment process with the various chemicals, the biomass undergoes certain changes (breakdown of LB components) that were shown in Figure 1. Therefore, it is necessary to study the efficiency of various pretreatment technologies through the changes that occur in LB characterization physically, chemically, and morphologically through several techniques used for research purposes. The most common methods utilized to study the compositional analysis of dissolved material (cellulose, hemicellulose, lignin, sugar yield, solid recovery, inhibitors, and products) of untreated and pretreated biomass are gravimetric analysis, Thermogravimetric analysis (TGA), and High-Performance Liquid Chromatography (HPLC) [91], [109]. Morphological characterization is visualized with the aid of microscopical techniques including Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Soft X-ray Tomography (SXT) [41], [110], [111]. The study of Crystallinity index and chemical structures of biomass components is calculated using Fourier Transform Infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR), Brunauer Emmett Teller (BET), X-Ray Diffraction (XRD), Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), and Response Surface Methodology (RSM) [41], [91], [110], [112], [113]. Table 4 briefly explains the purpose of a few techniques used to study the biomass after the pretreatment process.

Table 4: Techniques used to study the physical, chemical, and morphological structure of biomass after the pretreatment process

Techniques	Purpose of the Study
HPLC	Compositional analysis of components of LB, sugar yield, and product yield
Gravimetric analysis	Analysis of solid mass present in the sample
TGA	Analysis of thermal stability of the sample at different temperature
SEM	Surface morphological analysis of biomass
TEM	Morphological analysis of biomass
SXT	Study of porosity of the sample
BET	Study of pore volume and surface area of the sample using Nitrogen physisorption analysis
XRD	Study of crystallinity and chemical structures of biomass

Table 4: (Continued) Techniques used to study the physical, chemical, and morphological structure of biomass after the pretreatment process

Techniques	Purpose of the Study
FTIR	Study of crystallinity and chemical structures of biomass
ATR-FTIR	Study of crystallinity and chemical structures of biomass
NMR	Analysis of lignin dissolved in the sample
RSM	Optimization of reaction conditions

11 Future Outlook and Conclusion

This review covers the recent update concerning developments in the field of biomass pretreatment using chemicals to increase the sugar yield, and reduce inhibitors and expenses. The potential and new advances of many chemical methods have been studied in many works. The choice of chemical method mainly depends on the products to be obtained after the biorefinery process. The optimum parameters utilized in the chemical pretreatment play a significant role, thus, overseeing the ensuing sugar yield by hydrolysis. Furthermore, various benefits have likewise been accounted for the majority of the pretreatment strategies, which make them fascinating for industrial applications. Despite, there are many novel innovations in each pretreatment technology that includes the combined method to increase the sugar yield, there are still challenges to rectify through studies that are related to techno-economic and environmental drawbacks. So far, no chemicals have been discovered as the best option to utilize in the pretreatment of various biomass. Therefore, further investigation is required to develop a mechanism adapted to the chemical pretreatment method that results to meet the sustaining challenges.

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Author Contributions

D.J.: conceptualization, investigation, writing -original draft; N.K.: data curation, investigation, writing-

original draft. K.K.: writing - review and editing; M.S.: conceptualization, writing - review and editing, funding acquisition.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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