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Review Article

A Review on Chemical Pretreatment of Lignocellulosic Biomass for the Production of Bioproducts: Mechanisms, Challenges and Applications

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Abstract
Excessive dependence on fossil resources to supply the increased energy demands has led to unsustainable growth. Hence, there is a necessity to shift our reliance from non-renewable to renewable resources. In this scenario, lignocellulosic biorefinery gains its importance because lignocellulosic biomass can be converted into various value-added products. However, biomass pretreatment is necessary due to the recalcitrant nature of the biomass. Various pretreatment techniques are employed to convert biomass into a more amenable structure to be utilized in the further steps of biorefinery. Hence, this review concentrates on different chemical pretreatment techniques used currently on biomass along with their modes of action on the biomass. This review will provide a detailed concept of various chemical pretreatments and the recent developments in pretreatment techniques. Despite this, the limitations of the current pretreatment strategies and the difficulties in their industrial applications are also discussed, which could provide innovative ideas to overcome these issues.

Keywords: BCG economy, Biofuel, Biorefinery, Chemical pretreatment, Lignocellulosic biomass, Platform chemicals, Sustainable development

1 Introduction

Two main categorizations of bioproducts derived from plant or plant-derived wastes, industry-related wastes, animal wastes, and domestic wastes are conventional bioproducts, such as construction materials, forest products, pulp/paper and textiles, and emerging bioproducts, such as biomass energy (starch-based and cellulose-based ethanol, biobutanol, biohydrogen, biomethane, and biodiesel) bio-based adhesives, biochemicals and bioplastics [1]–[3]. Because of the concerns about the depletion of fossil-based energy resources and environmental conservation, biomass energy broadly receives the most attention from researchers. Thailand is notable as an agricultural country and exports industrial crops; therefore it also has abundantly massive crop residues that are mostly lignocellulose biomass. The complicated structure of lignocellulose mainly consists of cellulose 38–50%, hemicellulose 23–32%, and lignin 15–25% [4]–[6]. Each component of lignocellulosic biomass is connected via interpolymer linkages. Cellulose and

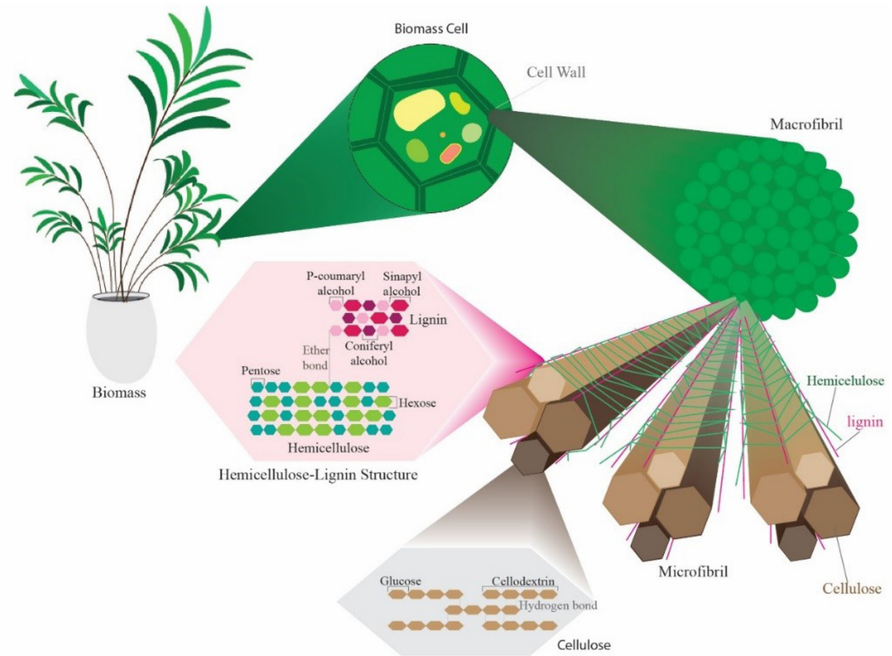

Figure 1: Basic structure of lignocellulosic biomass and its compositions.

hemicellulose are linked together by hydrogen bonds, whereas cellulose and lignin have ether and hydrogen bonds between them. Apart from this, hemicellulose and lignin are connected via ether, ester and hydrogen bonds [5], [7]. Among these linkages, the ether bond is considered the most important bond involved in the conversion of biomass to bioproducts because it connects lignin to cellulose [5], [8]. The basic structure of lignocellulose biomass depicts in Figure 1.

Cellulose is a linear polysaccharide that consists of several glucose monomers linked together via (β–1–4)-glycosidic bond [9]–[11]. The molecules of cellulose are arranged as stacks, which are stabilized by positioning hydroxyl groups axially to form microfibrils. The microfibrils, with the inside being hydrophobic and hydrophilic, externally, associate with each other to form macrofibrils [9], [12]. The main compositions of hemicellulose (xylan) consist of pentose and hexose sugars along with sugar acids [13], [14]. The amorphous and branched structure of hemicellulose is more susceptible to being degraded and modified during pretreatment processes and produces monosaccharides, oligosaccharides, and their derivatives [9], [10]. Lignin is an aromatic compound that binds to cellulose and hemicelluloses to cause a strong lignocellulosic materials structure [13], [15]. This review enlightens on the general operating conditions and mechanisms of delignification by different chemical pretreatment. In addition, new research, obstacles, and advantages are also the further aims of this review.

2 Pretreatment Process

In some circumstances, hemicellulose is placed in the context of recalcitrant constituents of lignocellulose biomass as same as lignin because it can inhibit the operation of some processes, such as bioconversion into nanocellulose, the nanofibrillation via electrospinning, and the polymer composite process [16], [17]. The recalcitrance constituents act as a physical barrier to obstruct the accessibility of chemical, physical, and biological attacks in the cellulose extraction process [4], [5]. The main functions of the pretreatment include delignification without affecting cellulose and hemicellulose content of biomass, removal of amorphous components in biomass, and increase in the surface area by reducing the particle size and increasing porosity of the biomass [5], [17].

3 Chemical Pretreatment

Among the pretreatment process methods comprising chemical, physical, biological, and combinational methods, chemical pretreatment (Figure 2) is the general method for the pretreatment of lignocellulose biomass and is commonly applied in many pilot and demonstration plants [17]. Chemical pretreatment is successful in a way that it helps in the efficient removal of lignin and hemicellulose in a short duration of time [5]. Unfortunately, a by-product is also produced during the chemical pretreatment process and requires expensive chemical recovery techniques that hinder its application on a large and industrial scale [4], [18]–[21]. Among the various chemical pretreatment methods employed to promote delignification, organosolv, deep eutectic solvents, and alkali pretreatments are widely applied for this purpose [22]. The characteristics of these various chemical pretreatment methods, consisting of the mode of action on the biomass, mechanism, shortcomings, and advantages are summarized in Table 1.

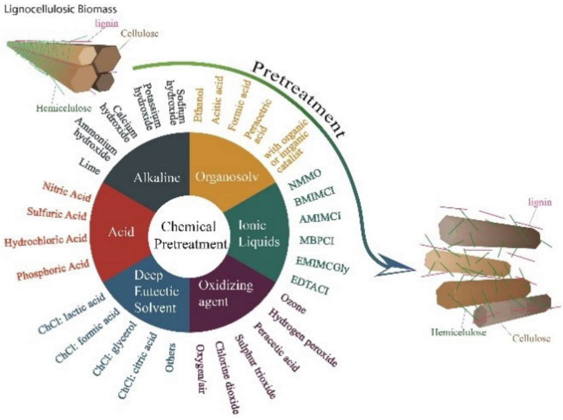

Figure 2: Schematic representation of pretreatment effect on lignocellulosic biomass and example reagents of different chemical pretreatment.

3.1 *Acid pretreatment*

In the low pH operation of pretreatment, almost all hemicelluloses are solubilized and removed from the solid material, meanwhile, the cellulose and lignin components are not affected, leading to the accessibility of enzymes in the subsequent hydrolysis process [23]–[25]. In basic theory, acid pretreatment interrupts the chemical bonds in the lignocellulosic biomass [4], [6]. The hydronium ions generated during the acid treatment lead to the cleavage of inter and intra-polymer glucosidic linkages leading to the release of monomeric sugars [5].

Table 1: Mechanism and effect of different chemical pretreatment methods on lignocellulosic structure

Method	Action/Mechanism	Advantage	Disadvantage	Ref.
Acid	Hemicellulose removal/The hydronium ions are generated and breaked down the polymer glucosidic linkage.	Efficiency for lignin removal. High sugar yields.	Need corrosion –resistant equipment. Possible formation of inhibitors.	[5], [9], [48]
Alkaline	Lignin removal/ Causing the saponification of intermolecular ester bonds leads to the disruption of lignin structure.	Less energy consumption. Not require detoxification.	Wastewater generation by washing. An expensive alkaline catalyst.	[5], [28], [36]
Organosolv	Hemicellulose removal and delignification/ Hydrogen ions is generated to hydrolyze the internal bonds of lignin and hemicellulose through the cleavage of ether and ester bonds.	Recovery of relatively pure lignin. No need to initiate mechanical pretreatment.	High cost. Difficulty in providing for the washing process. Need high caution operation because of fire and explosion hazards.	[23], [28], [31], [41], [49], [50]
Oxidizing agent	Lignin removal/ Lignin is oxidized to carbon dioxide, carboxylic acids, and water during the wet oxidation pretreatment.	Efficient lignin removal. Reducing energy demand. No generated toxic.	High cost of oxidants. More energy requirement. Loss of hemicellulose and cellulose.	[23], [28], [51]
IL	Lignin and hemicellulose removal/ The anions present in the IL form a hydrogen bond with the cellulose and cause the breakage of bonds within the cellulose.	Efficient dissolution of biomass, almost 100% recovery possibility.	Expensive due to the very high recovery cost. Difficult to separate hydrophilic IL and monomeric sugars in water. High energy requirement.	[13], [23], [31], [49], [52], [53]
DES	Lignin and hemicellulose removal/ cleaving the ether bonds within lignin and causing the dissociation of protons leaded to hemicellulose removal	Low volatility. Non-toxicity. High thermal stability.	High viscosity	[13], [23], [54]

The acid pretreatment methods, namely dilute acid pretreatment and strong acid pretreatment, have been used in the lignocellulose biorefinery for producing fermentable sugars [4]. Acid pretreatment types that are the most reputable and mainly used are CH_3COOH, HCl, and H_2SO_4 because of their low cost and ability to alter the crystallinity of cellulose [4], [5], [9], [26]. Unfortunately, inhibitors belonging to the groups: sugar-derived aldehydes (furfurals, 5-hydroxymethylfurfural), short-chain organic acids (acetic acid, formic acid), and phenolic compounds (ferulic acid) are generated by the dehydration of pentose and hexose sugars during acid pretreatment [4], [27]. Therefore, acid pretreatment needs two further steps: the detoxification process for removing the inhibitors from the reaction mixture, and the acid recovery process required more energy consumption because of the difficulty of removal from the hydrolysate [5], [9].

3.1.1 Dilute Acid Pretreatment (DAP)

During the DAP process, solubilized hemicellulose, mainly xylan, is hydrolyzed to produce monomers, furfural, HMF and other products [28], [29]. DAP operates in two different ways: the first, dilute acid (0.1%) at high temperatures (100–210 °C) for a short time (20 min), and the second way, at low temperatures e.g., 120 °C for a longer time (30–90 min) [25], [30], [31]. In the procedure of DAP operation, the lignocellulosic biomass in an aqueous solution is introduced into the stainless steel reactor, followed by heating the reactor. Subsequently, the reaction is initiated by adding the acid at the desired temperature and specified time [9], [32].

3.1.2 Strong Acid Pretreatment (SAP)

At a high acid concentration (30–70%), pretreatment operates under mild conditions of low temperature (30–60 °C) for a short duration of time [25], [30], [31]. Because of lower temperature operations in SAP, energy consumption is less than a DAP. However, the SAP also producs inhibitors such as furan derivatives, phenolic acids, and sugar-derived aldehydes. Furthermore, corrosion-resistant equipment and further detoxification are necessary for the downstream process [4], [11], [25]. These inhibitors cause the breakage of DNA and reduce the RNA synthesis of microorganisms in the fermentation process, which hinders enzymatic activities [25], [33].

DAP is more suitable than the SAP method because of more sugar yield and less energy consumption [4]. Furthermore, DAP also lowers the effects of the process such as toxicity, corrosiveness, hazardous processes, acid consumption, and inhibitor generation preventing the corrosion of the equipment and easier scale-up [11], [24]. However, because the DAP method operates under higher temperatures, it needs high energy for the overall process [25]. For decreasing inhibitor production, a potential option is replacing traditional acid with weak and organic acids [11].

The effects of two different DAPs on melon seed husk (MSH) were studied by comparing the physical and chemical structure of MSH after the pretreatment with sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). The pretreatment was conducted at 90 °C for 1 h using 3.5 M acid concentration/20 g dry biomass [6]. The results indicated that acid treatment had efficiency in the demineralization of MSH, while it did not affect its chemical structure. Moreover, the result showed H_2SO_4 was more effective on MSH than HCl. Glycolic acid pretreatment of eucalyptus was investigated to solubilize hemicellulose [34]. The results showed a higher yield of xylose (56.72%), followed by a hemicellulose yield of 65.48%, having a purity of 72.08%. The glycolic acid was also recovered at a rate of 91%. A comparison of the glycolic acid with formic acid showed a 10.33% increasing in the yield of xylose, and an 11.08% lignin reduction. Furthermore, glycolic acid pretreatment on lignocellulosic components did not affect the cellulose structure; instead, the pretreatment affected the hemicellulose and also inhibited the polymerization capabilities of lignin. Optimum conditions for sulfuric acid pretreatment of sugarcane bagasse were evaluated via a mathematical model using the Box-Behnken design (BBD) [35]. The results showed the ideal pretreatment conditions, including acid concentration (3.50%), temperature (136.08 °C), and time (75.36 min), led to a reducing sugar of 4.41 mg/mL. The aforementioned research are concisely mentioned in Table 2, involved in pretreated conditions and process efficiency of various biomass for this acid pretreatment method and other chemical pretreatment methods.

Table 2: Summary of the efficiency of different chemical pretreatment methods for various lignocellulosic biomass

Biomass	Chemicals	Pretreatment Parameters	Process Efficiency	Ref.
Melon seed husk	H_2SO_4, HCl	90 °C, 1 h, 3.5 M acid, 2 g Biomass	Lignin decreased from 0.29% to 0.02% (H_2SO_4) and 0.5 (HCl)	[6]
Durian peel	H_2SO_4	2.75% H_2SO_4, Biomass loading: 2%, 127.14 °C, 74.13 min	Sugar yield 73.6%	[95]
Eucalyptus	Glycolic acid	5.40% acid, 140 °C, 3 h	Xylose yield 56.72%, recovery rate 91%, hemicellulose yield 65.48%	[34]
Sugarcane bagasse	H_2SO_4, AP, APAA, SC	3.50% acid 136.08 °C, 75.36 min	Reducing sugar 4.41 mg/mL, AP and APAA affect to release of cellulose but SC does not affect pure cellulose structure	[35], [66]
Cassava rhizome (CR)	$Ca(OH)_2$, $Mg(OH)_2$, KOH, NaOH	10, 20, 30 wt.% dry CR, 120 °C, 1 h	Maximum cellulose (78.61%) achieved from 30 wt.% KOH	[38]
MCH* and YCH*	NaOH	5% w/v of NaOH , 121 °C, 40 min	Sugar yield of MCH is 71.23% and YCH is 89.49%	[39]
Rice straw	NaOH	0.5–2% of NaOH concentration in a ratio of 1:20	Maximizing holocellulose generation of 80.1% at 1.5% of NaOH	[40]
Wheat straw	HCOOH and acetic acid mixture	60–80% v/v of acid mixture, 70–90 °C, 20–40 min	Conversion efficiency: 70.22 % (684 mg/g), ethanol yield of 40.85%	[46]
Potato crop residues	Ethanol with H_2SO_4 as the catalyst	50% v/v of ethanol, 180 °C, 20–40 min	Maximum glucose yield of 74.6%	[47]
unbleached bamboo kraft pulp (UBKP)	Ozone	liquid to solid ratio (1.2:5 w/w) 30 °C, pH: 2.5,	Lignin removal of 9.96 wt% and reduction in DP to 1210	[64]
Rice husk	HP, CHPA	Biomass: H_2O_2 of 1:10 (w/v), 30–80 °C, 48 h	CHPA achieved 6.58 g glucose/L	[65]
Date palm waste biomass (DPWB)	20 % NH_3, IL (EMIMAc)	DPWB:NH_3 (1:10), 80 °C, 12 h DPWB:EMIMAc (3:97), 160 °C	Substrate conversion efficiency of IL (68.01%), substrate conversion efficiency of alkaline (62.09%)	[85]
Corn cobs and corn stalks	TBPH ionic liquid	20–80 °C, 0.5–2 h, TBPH of 10–40 wt%	Sugar yield for corn cob: 90.75%, sugar yield of stalk: 80.84%	[86]
Triarrhena lutariori-paria (TL)	ChCl-based DESs	Biomass loading of 1:25, 110 °C, 5 h	Hemicellulose and lignin removal achieved over 80% and 67% respectively.	[92]
Masson pine	ChCl:LA	ChCl:LA (1:10), 130 °C, 4 h	Lignin removal (81.2%), purity of recovered lignin (92.5%)	[93]
Bamboo residues	ChCl-oxalic acid-ethylene glycol	solid to liquid ratio (1:10), 110 – 140 °C, 6 h	Glucose yield of 65.98%	[94]
Napier grass	ChCl/lactic acid (1:4)	Biomass loading of (1:6.5, w/w), 80 °C, 5 h	Glucose yield of 87.09%	[96]

* MCH is mature coconut husk, YCH is young coconut husk

3.2 *Alkaline pretreatment*

One of the main chemical pretreatment processes is alkaline pretreatment, which is known for its delignification capacity without affecting the cellulose and hemicellulose fractions [5], [13], [28]. Delignification is a physical and chemical pretreatment mechanism to improve the reactivity of remaining polysaccharides during biomass conversion [23], [28]. The alkaline reagent causes the saponification of intermolecular ester bonds of biomass polymer complex and promotes the degradation of the side chain of glycosides. This leads to the disruption of lignin structure, swelling of cellulose, and partial solvation of hemicellulose ions [28], [31], [36]. Thus, the reaction enhances the internal surface area along with a decrement in the crystallinity of cellulose and the degree of its polymerization [29].

Alkaline pretreatment could be operated under lower temperatures and pressure, but it spends longer times than other pretreatment technologies [28]. Well-known alkaline agents of pretreatment technologies are NaOH, KOH, $Ca(OH)_2$, and ammonia [4], [5]. Because the process is operated under mild conditions, it requires less energy and does not need the detoxification process [5]. Alkaline pretreatment results in two fractions, one of which is a cellulose-rich solid fraction and the other fraction including dissolved hemicelluloses, lignin, and some unreacted inorganic chemicals in liquid form [31].

Effects of alkaline pretreatment on cassava rhizome (CR) components were studied using three alkaline agents, namely $Ca(OH)_2$, $Mg(OH)_2$, KOH, and NaOH, at different concentrations of 10, 20 and 30 wt.% dry CR pretreated using hot compressed water at 120 °C for 1 h [37]. The results showed that 30 wt.% KOH achieved maximum cellulose content and 30 wt.% NaOH received the lowest crystallinity. The aim of alkaline pretreatment (NaOH) is to degrade mature coconut husk (MCH) and young coconut husk (YCH) for provided in subsequent hydrolysis process using 10% enzyme (Accellerase® 1500) loading for 24 h [38]. NaOH was successful in removing the lignin from MCH (20.15%) and YCH (31.17%). This resulted in attaining reduced sugar content of 19.17 g/L and 24.33 g/L from MCH and YCH, respectively. Furthermore, NaOH was used for the pretreatment of rice straw (RS) [39]. The results indicated that among various NaOH concentrations of 0.5%,1.0%,1.5%, and 2%, NaOH concentrations of 1.5% had the most potential for producing holocellulose.

3.3 *Organosolv pretreatment*

The organosolv pretreatment method generally applies a wide range of organic solvents such as methanol, ethanol, acetone, organic acid (e.g., formic and acetic acid), ethylene glycol, and tetrahydrofurfuryl alcohol to the pretreatment process. In addition to this, sometimes organic acids (e.g., acetylsalicylic, oxalic, and salicylic) or bases (e.g., sodium hydroxide and lime) are also used as catalysts, in solubilizing hemicellulose and extracting lignin [40]–[42]. The presence of organic acids in organosolv pretreatment provides hydrogen ions to hydrolyze the internal bonds of lignin and hemicellulose through the cleavage of ether and ester bonds. This promotes the removal and dissolution of lignin as well as the degradation of hemicellulose to smaller compounds [13], [23], [43]. Organosolv pretreatment results in the biomass fractionation into 3 fractions, including pure cellulose fraction, hemicellulose fraction with hexose and pentose sugars, and lignin fraction with high purity [31].

Organosolv pretreatment operates under mild conditions and does not need to initiate a mechanical pretreatment. The recovery of organic solvents to the pretreatment process is possible and can be easily achieved by distillation. The operating conditions depend on the type of lignocellulose materials. In general, the organosolv process operates under a high temperature of 100–250 °C, an ethanol concentration of 35–70% (w/v), a liquor-to-solid ratio of 4:1–10:1 and a pH range of liquor from 2.0 to 3.8 for a long time (30–90 min) [11], [28], [44]. In the organosolv pretreatment process using an inorganic acid in the context of catalysts, hemicellulose is hydrolyzed to increase the availability of cellulose for further processes [23], [45]. However, the pretreated solids are required to be washed in organic solvents before washing with water to prevent reprecipitation of dissolved lignin [28].

A mixture of formic acid and acetic acid in the equal fraction was used in organosolv pretreatment to investigate the optimum conditions of wheat straw biomass [46]. The operating conditions were exposure time (20–40 min), pretreatment temperature (70–90 °C), and acid concentration (60–80%, v/v). The results showed optimum conditions : a temperature of 79.5 °C, an acid concentration of 69.5%, and an exposure time of 28.80 min, which resulted in a conversion efficiency of 70.22% (684 mg/g), and an ethanol yield of 40.85%. The study of ethanol as organosolv pretreatment of potato crop residues (PCR) was considered to improve product yields [47]. The use of H_2SO_4 (1% w/w) as a catalyst with ethanol of 50 and 75% v/v at different temperatures (120, 140, and 180 °C) was also evaluated. The maximum glucose yield of 74.6% was obtained under temperature 180 °C, ethanol of 50%, and catalytic pretreatment.

3.4 *Oxidizing agent pretreatment*

The oxidative pretreatment of lignocellulose materials uses ozone and other oxidizing agents such as hydrogen peroxide (H_2O_2), peracetic acid ($C_2H_4O_3$), sulfur trioxide (SO_3), chlorine dioxide (ClO_2), and oxygen/air as catalysts [23], [28]. Ordinarily, the reactor of oxidative pretreatment operates under relatively low temperatures varying from 170 to 200 °C and a short duration of time (10–20 min) [28], [55]–[57]. This exothermic process occurs when air or oxygen is added at a temperature above 170 °C, leading to reducing the total energy demand [28]. During the wet oxidation pretreatment, lignin is oxidized to carbon dioxide, carboxylic acids, and water; moreover, the crystalline cellulose gets exposed and leads to increasing the accessibility of enzymes in the hydrolysis process [28], [51], [58], [59]. Among the oxidizing agents, hydrogen peroxide is the most important as the hydrogen peroxide products are hydrogen and oxygen that are not an inhibitor of the subsequent process [31], [60].

The process has the efficiency in removing lignin ranging from 50 to 70% depending upon the type of biomass used in the pretreatment [28], [61]. Nevertheless, oxidizing agents are expensive, requiring both high energy and a large amount of ozone. This obstructs the development of wet oxidation technologies on a large scale [23], [28], [33], [49], [62]. The solubility and removal of lignin for oxidative pretreatment have two drawbacks: 1) the loss of hemicellulose and cellulose, 2) the production of inhibitors, which obstruct the conversion of hemicelluloses and cellulose to ethanol [29], [30], [31], [63].

The combination of ozone pretreatment and enzymatic hydrolysis was studied to enhance the fiber flexibility of unbleached bamboo kraft pulp (UBKP) [64]. This study showed a reduction in the lignin content from 14.46 wt.% to 9.96 wt.%, along with a reduction in the Degree of Polymerization (DP) to $n = 1210$ after ozone-cellulase treatment. The comparison of hydrogen peroxide (HP) and combined hydrogen peroxide–aqueous ammonia (CHPA) pretreatments was investigated to enhance the hydrolysis of rice husk [65]. The pretreatment used 3% H_2O_2 solution for a solid loading of 1:10 (w/v) at a temperature of 30–80 °C for 48 h and then added 20% (v/v) aqueous ammonia solution. The efficiency of lignin removal was converted from 48.25 to 66.50% of HP and from 72.22 to 85.73% of CHPA. The optimum glucose production of 6.58 g/L was obtained from pretreated CHPA. Three oxidative pretreatments, using alkaline hydrogen peroxide (AP), alkaline/peracetic acid (APAA), and sodium chlorite (SC), were aimed to enhance the lignin removal from sugarcane bagasse [66]. AP and APAA led to the disappearance of the middle lamella and released cellulose fibers with etching, deformation, and fracture of the cell wall structure. SC had a severe effect on the surface morphology of sugar bagasse, but it had no significant effect on pure cellulose structure.

3.5 *Ionic Liquid (IL) pretreatment*

Ionic liquids (IL) are considered green solvents and have gained much attention from researchers in recent years [67], [68]. IL are salts including two parts as follows: an organic cation, which consists of organic cores, such as imidazolium, phosphonium, pyrrolidinium, cholinium, etc., and an inorganic anion [13], [52], [69], [70]. Dilution of IL with water during the pretreatment reaction is carried out to enhance the hydrolysis efficiency to obtain glucose monomers. [33], [71]. The oxygen and hydrogen atoms present in the hydroxyl groups of cellulose form an electron donor-electron acceptor complex (DA), which can interact with IL and enables cellulose solubilization [28], [72]. Ionic components in IL have a known effect on the solubility and stability of cellulose, in which the anions present in the IL form a hydrogen bond with the cellulose and cause the breakage of bonds within the cellulose [23], [73]–[75]. This causes the disintegration of the cellulose structure by swelling the cell wall, thereby reducing its crystallinity. IL thus helps in enhancing the solubility of cellulose and lignin combined with partial hemicellulose removal [23], [31], [76].

Recovering the solubilized cellulose from the pretreatment liquid requires the addition of some anti-solvents, such as ethanol, acetone, methanol, or water, under mild conditions [77], [78]. The recovered cellulose would have decreased crystallinity in addition to the similar DP and polydispersity as the initial cellulose. Moreover, there is a nearly 100% possibility of recovering used IL from the pretreatment liquid [28], [79]. After the washing process, any remnants of IL lead to the inhibition of enzymes and organisms in the fermentation process via the denaturation of enzymes [80]–[82]. It can also block the active sites of enzymes leading to the destruction of the aqueous phase surrounding the enzyme surface [13], [73], [83], [84].

To compare the pretreatment of alkaline (20% NH_3) and IL (1-ethyl-3-methylimidazolium acetate

(EMIMAc)) of date palm waste biomass (DPWB) was investigated [85]. All results, which comprised the biochemical methane potential (BMP), the substrate conversion efficacy (SCE), and morphological changes, indicated that IL pretreatment enhanced methane production better than the alkali pretreatment. Another study has investigated the efficiency of tetrabutyl phosphorus hydroxide (TBPH) aqueous solution, which is a strong proton acceptor, in pretreating corn cobs and corn stalks [86]. The sugar yield for corn cob and corn stalk was 90.75% and 80.84%, respectively. Both hemicellulose and lignin were removed, while the cellulose crystal was intact.

To overcome the limitation of IL utilization, namely high cost, caused to apply for industrial levels infeasibly, IL is mixed with inorganic salts, such as NaCl, KCl, $MgCl_2$, $CaCl_2$, $NaNO_3$, $ZnCl_2$, $FeCl_3$, KNO_3, $Mg(NO_3)_2$, etc. to decrease the IL load in pretreatment process [87], [88]. The six inorganic salts consisting of NaCl, KCl, $MgCl_2$, $NaNO_3$, KNO_3 and $Mg(NO_3)_2$ were mixed with IL, 1-ethyl-3-methyl-acetate (Emim-AC) for the rice straw pretreatment at 120 °C for 90 min [87]. The results showed that the mixture of Emim-AC and 1% NaCl obtained with the highest reducing sugar of 3.099 mg/mL. Moreover, rice straw was also pretreated with the mixture of 40% IL (1-ethyl-3-methylimidazolium chloride ($[C_2mim]Cl$)) + 53% water + 7% inorganic salts (K_2CO_3) at 110 °C for 1 h [89]. The results achieved a sugar yield of 92.07%. The results of both research works were similarly achieved, significantly reducing the cost of IL pretreatment [87], [89].

3.6 *Deep Eutectic Solvent (DES) pretreatment*

DES has received significant attention in the past few years due to its environmental friendliness. Despite this, DES also possesses unique properties of high polarity, good miscibility, and delignification capability for different biomass [25], [90]. DESs are a group of the eutectic mixture of bases and Lewis or Brønsted acids; these mixtures consist of various kinds of anionic and cationic species [13]. DES and IL have similar properties, therefore DES is regarded as a new class of IL [91]. DES is a mixture of two- or more components, including; a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) [23]. These compounds are mixed at medium temperature to produce DESs. Even though DES is known for its delignification ability, it can also help remove hemicellulose caused by the dissociation of protons. A different group of HBD can have different effects on DES pretreatment. For instance, HBD with strong electron-withdrawing groups can enhance the pretreatment performance, whereas hydroxyl or amino groups reduce the process efficiency. Among DESs, choline chloride is the most commonly studied HBA as it is frequently used in animal feedand is thus safe in the health aspect [13]. Other factors, like low cost, ease of synthesis, and less expensive ingredients have resulted in the replacement of conventional IL with DES [13], [25].

A study was conducted to investigate the pretreatment of Triarrhena lutarioriparia (TL) with 7 different ChCl-based DESs [92]. Among the various DES tests, ChCl-oxalic acid dehydration (2:1) displayed better pretreatment efficiency. The effectiveness of pretreatment was determined by uniform design (UD) experiments to achieve maximum enzymatic digestibility of 83.71%. Despite this, hemicellulose and lignin removal of more than 80% and 67% were also achieved in this pretreatment. The optimum conditions for choline chloride/lactic acid (used as DES) pretreatment of masson pine were a molar ratio of 1:10 and pretreatment of 130 °C for 4 h [93]. The study revealed that the recovered lignin (72.3%) had a purity of 92.5%. Another study on the pretreatment of bamboo residues with three-constituent DES (3c-DES), namely choline chloride-oxalic acid-ethylene glycol, could achieve a glucose yield of 65.98%, which was 1.7 times more than 2c-DES pretreatment [94].

4 Combinational Pretreatment Strategies

The pretreatment with a steam explosion (SE) in the first step and subsequent alkaline pretreatment (NaOH) for green coconut fiber (GCF) helped to increase ethanol concentration [97]. Moreover, it could achieve a higher hydrolysis yield of 54.74%, with a total reducing sugar of 29.17 g/L and a glucose concentration of 16.65 g/L. The results revealed that the combination pretreatment achieved more sugar and ethanol yield than individual pretreatment. Xylo-oligosaccharides (XOS), which were the product of acetic acid (AC) hydrolysis from poplar, also generated a lignin-rich fraction [22]. Further pretreatment of lignin-rich poplar with optimized hydrogen peroxide-acetic acid (HPAA) of 10% at 120 °C for 10 min and followed by sodium hydroxide-urea (SU) successfully removed acetyl groups and reducing lignin content by about 21.1%. This pretreatment has helped remove lignin, which has resulted in enhancing the glucose yield from 21.4% to 95.5%, saving up to 90% of HPAA consumption and taking a short time for hydrolysis. Another study evaluating the usage of O_2 and H_2O_2 as co-oxidants for alkaline-oxidative pretreatment revealed a higher sugar yield by using low H_2O_2 loading of 2% [84]. Furthermore, it also achieved better biomass fractionation than using H_2O_2 alone in pretreatment.

5 Commercial Application

For the applications of dilute acid pretreatment, bioethanol and biogas are the main final products of DAP applied to commercial and demonstration plants [5], [84], [98]. The application of concentrated acid pretreatment on an industrial scale is almost impossible as it causes corrosion to the equipment and difficulty in recovering the catalyst leading to high operational and maintenance costs [11], [99]. Alkaline pretreatment, being able to remove lignin, can be used to pretreat biomass with less lignin, such as hardwood, herbaceous crops, and agricultural residues [13], [28], [60], [100], [101]. The alkaline pretreatment is the traditional method to apply in the process of pulp, paper, and high-quality journal paper production [8], [13], [28]. Organosolv pretreatment method is closest to the biorefinery process because the products of all biomass components change to fuel and value-added chemicals achieved in the pure form [11], [31], [42]. For oxidative pretreatment, the main restriction of scaling up to industrial levels is the high cost of oxidizing agents [31]. IL pretreatment process has some obstacles such as separating and recovering the mixture of carbohydrates, lignin, and proteins to scale up in large-scale biorefineries [31]. For the potential application of DESs, component fractionation in a biorefinery process is promising [13]. DES, being very versatile, has already been used in different industries of electrochemistry, pharmaceuticals, fossil fuels, food, and feed production [13], [102].

6 Conclusions

The review has focused on detailing different chemical pretreatment techniques that can be used to pretreat the biomass, along with their mode of action. Even though all pretreatment methods help in reducing the recalcitrance of the biomass, each pretreatment technique has its advantages and disadvantages. In comparison, among the various chemical pretreatments, DES pretreatment is widely studied due to its ability to remove lignin without inhibitor production and its eco-friendliness. Despite this, researchers have also initiated studies with combinatorial pretreatment strategies to maximize the sugar yield. However, more studies are required to understand its limitations and confirm its industrial-scale application. This review can thus help in understanding the current pretreatment techniques and their limitations, and help to improve them by tackling their limitations.

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Author Contributions

S.A.: conceptualization, investigation, manuscript preparation; E.P.: reviewing and editing; validation; M.S.: conceptualization, reviewing and editing; funding acquisition; T.K.: reviewing and editing; S.A.: reviewing and editing; U.H.: reviewing and editing; P.Y.: reviewing and editing; A.T.: investigation, reviewing and editing

Conflicts of Interest

The authors declare no conflict of interest.

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