Review Article

Chemical Pretreatment of Lignocellulosic Biomass for the Production of Bioproducts: An Overview

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Abstract

Lignocellulosic biomass has attracted great interest from researchers. It was due to the abundance of this valuable material which can be converted into value-added materials such as nanocellulose, biocomposites, bioelectricity, biohydrogen and biosugars. Lignocellulosic biomass is consisting of the three major components which are cellulose, hemicellulose and lignin. In order to utilize lignocellulosic biomass for bioproducts manufacturing, they need to be pretreated prior to further processing. Pretreatment can be carried out either by mechanical, chemical, biological or combination of all these methods. Chemical pretreatment is the common method used to pretreat the lignocellulosic biomass in order to completely or partially remove the components. During the past few years, a large number of chemical pretreatment including lime, acid, steam explosion, sulfur dioxide explosion, ammonia fiber explosion, ionic liquid and others have been discovered to be efficient pretreatment of biomass. Several types of chemical pretreatment of fibers and their future direction and also challenges were tackled in this review. This review could be beneficial for future directions in the pretreatment of fiber for the development of several products.

Keywords: Lignocellulosic, Biomass, Chemical pretreatment, Bioproducts

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1 Introduction

In the 21st century, when humans become aware of environmental conservation, applications of renewable resources become more and more important for their daily life since they are friendly to nature. In recent years, there are raising concerns by the public in creating environmental sustainability of the industry through utilisation of biomass [1]–[3]. Various biomass such as oil palm biomass, bamboo, sugar palm, wood, wheat straw and bagasse are suitable candidates for development of bio-based products such as biocomposites, biosugars and nanocellulose [4]–[9]. It is a similar concept with today's petroleum refinery, which produces various types of fuel and product from petroleum. In this process, each technology yields different types of co-products and by-products, which are useful and marketable. Thus, the main challenge is to discover processing technologies that can collect and convert current biomass into products with higher value.

The barrier to the production of valuable materials from lignocellulosic is the structure of this material which has evolved to resist degradation due to crosslinking between the polysaccharides (cellulose and hemicellulose) and the lignin via ester and ether linkages [10]. The main goal of any pretreatment is to alter or remove structural and compositional impediments to increase yields of intended products which is cellulose [11]. For an example, the presence of hemicellulose and lignin in the lignocellulosic materials limit the conversion of cellulose into nanocellulose and also will influence the properties of biocomposites. Pretreatment of fibers is important to be done in order to achieve one or more of the following objectives [12], [13]:

- Removing undesirable fiber constituents
- Roughening of the fiber surface
- Separating individual fiber from their bundles
- Modifying the chemical nature of the fiber surface
- Reducing the hydrophilicity of the fiber
- Cost effective
- Avoid degradation or loss of carbohydrate

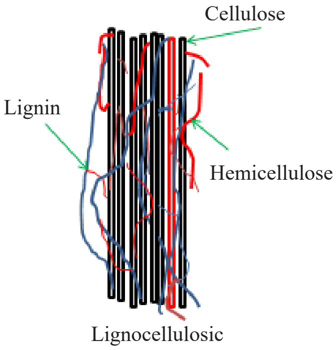

Figure 1: Basic structure of lignocellulosic material.

By referring to Table 1, several methods were developed to pretreat lignocellulosic material by the use of chemical, enzymes, biological, and physical methods with several purposes. Chemical pretreatment is the most common methods for lignocellulosic biomass components degradation and modify or remove lignin and hemicellulose [14], [15].

2 Lignocellulosic Components

Lignocellulosic component of plant biomass consists of cellulose $(C_6H_{10}O_5)_n$, hemicellulose $(C_5H_8O_4)_m$ and lignin $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_x$ which incorporated to form a strong cellulose-hemicellulose-lignin complex within the plant material [10], [16]. Figure 1 shows the interaction of cellulose, hemicellulose and lignin in the fiber.

Table 1: Examples of pretreatment for lignocellulosic materials

Pretreatment	Findings	References
Chemical	Successful removal of lignin and hemicellulose from fiber.	[18]–[25]
Biological	45–75% and 65–80% holocellulose and lignin degradation, respectively by Phanerochaete chrysosporium.	[10]
Enzymatic	Enzymatic pretreatment by endoglucanase, xylanase and pectinase improved ~89% of biogas production from sugar beet pulp.	[26]
Physical	a) Steam explosion for pretreatment of agricultural residues and hardwoods.	[27]
	b) Microwave radiation-assisted alkali pretreatment removed hemicellulose and lignin.	[27]
	c) Hydrothermal pretreatment of fiber.	[11]
	d) Super-heated steam pretreatment for hemicellulose removal.	[18], [21]
Combined pretreatment	a) Chemical-physical pretreatment of hemp fibers recovered ~80% of cellulose.	[28]
	b) Combined alkaline hydrothermal and ball milling reduced hemicellulose and enhanced enzymatic hydrolysis of oil palm fibers.	[16]

Table 2: Chemical composition of natural fibers biomass

Biomass	Lignocellulosic Components (%)			Reference
	Lignin	Hemicellulose	Cellulose	
Rubber wood	45	20	29	[31]
Bamboo	46.4	27.1	25.0	[32]
Flax	73	13	5	[33]
Kenaf	63.5	17.6	12.7	[34]
Oil palm mesocarp fiber	24.9	36.7	38.4	[21]
Oil palm frond	13-37	34-38	40-50	[17]
Oil palm empty fruit bunch	14.2	30.9	44.4	[35]
Oil palm trunk	18-23	12-17	29-37	[17]

It is well known that chemical constituents of natural fibers significantly vary due to their diverse origins and types [17]. Table 2 shows different lignocellulosic composition in several natural fibers biomass.

Generally, the cellulose, hemicellulose and lignin contents in a typical lignocellulosic fall within the range of 30–60, 20–40, and 15–25%, respectively.

Cellulose is the most abundant component in biomass and finds applications in many spheres of modern industry [29]. Cellulose is a high molecular weight linear homopolymer, comprising β-D-glucopyranosyl repeating units joined by 1-4 glycosidic linkages [30]. It can be found in a linear chain of anhydro-glucose monomer units connected by 1-4 β-linkages and stabilised at the end terminal with non-reducing and reducing sugar units. The properties of the cellulose chain can be attributed to reactive –OH groups that reside on position C-2, C-3, and C-6. It is noted these hydroxyl groups and their ability to form hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. The hydrogen bonding of many cellulose molecules to each other results in the formation of microfiber that can interact to form fiber. Cellulose fibers are being used for several applications because of so many advantages such as abundantly available, low weight, biodegradable, cheap, renewable, low abrasive nature, and exhibit good mechanical properties.

Hemicellulose is a second major component of lignocellulosic that consists of short chains of different polysaccharides such as xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan that are held together by β-(1,4)- and/or β-(1,3)-glycosidic bonds. In contrast to cellulose, hemicellulose is readily degradable into monosaccharides due to low degree of polymerization and non-crystalline nature and thereby widely used in industrial applications such as drug carriers, hydrogels, and cosmetics.

Lignin forms a protecting boundary by covalently linking to the cellulose and hemicellulose which enhances the recalcitrance of the lignocellulosic biomass. It is a complex, three-dimensional cross-linked polymer that consists of phenyl propane structural units and vary depending on the substitute of the methoxyl groups present in the aromatic rings and are linked to each other by aryl ether linkages e.g., β-O-4, α-O-4 and carbon-carbon bonds e.g., 5–5, β-β. Three basic units that constitute the lignin polymer are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S).

3 The Importance of Chemical Pretreatment for Several Applications

Chemical pretreatment of lignocellulosic materials is commonly employed in many pilot and demonstration plants because it is ideal for materials with low lignin content. This pretreatment is necessary for the conversion of biomass into several bioproducts such as nanocellulose, biocomposites and biosugars. Chemical pretreatment is often utilized to extract the corresponding bio-polymeric constituents of lignocellulosic biomass prior biochemical conversion as lignocellulosic biomass is considered recalcitrant in nature since it is resistant to chemical degradation (Figure 2). The pretreatment includes introducing organic or inorganic compounds to disrupt the biomass structure by interfering with the intra- and interpolymer linkages of main organic components [36]. Also, several compounds have been found to have a significant influence on the

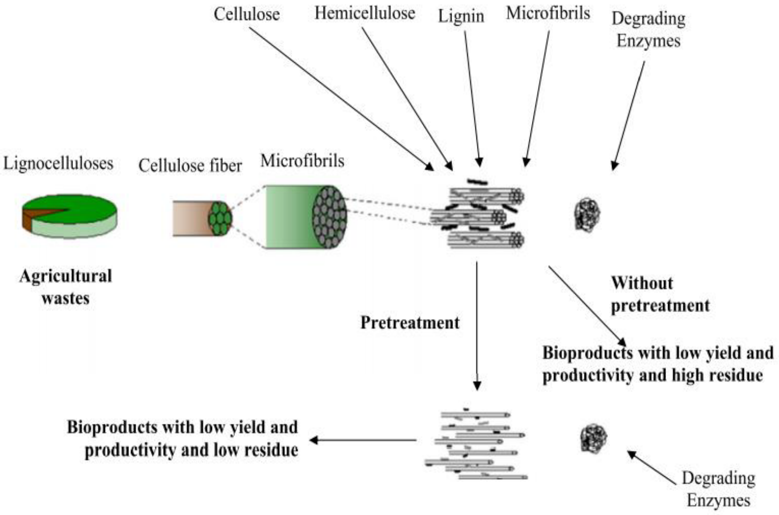

Figure 2: Effect of pretreatment on the properties of bioproducts. Image adapted from [37].

native structure of lignocellulosic biomass, create zero harmful residues for downstream processes that occur at room temperature and pressure [37].

3.1 *Nanocellulose*

Nowadays, nanocellulose gets high attraction from research and industries. Nanocellulose is a natural nanomaterial which can be extracted from plant cell wall. With its nanometer size in diameter, nanocellulose consists of attractive properties such as high strength, excellent stiffness, and high surface area. Nanocellulose can be used in various fields in our life, such as biomedical products, nanocomposite materials, textiles, adsorbent and military [38]–[46].

The barrier to the production nanocellulose from natural fibers is the structure of lignocellulose which contains hemicellulose and lignin. The presence of high amount of hemicellulose and lignin in the lignocellulosic materials limit the conversion of cellulose into nanocellulose. The main goal of any pretreatment is to alter or remove structural and compositional impediments to increase yields of intended products which is cellulose [5], [16], [47]. The chemical pretreatment can ensure that cellulose materials can react more consistently in subsequent fibrillation treatments, resulting in good nanocellulose properties.

Based on previous research, the presence of high amount of lignin and hemicellulose inhibit the nanofibrillation of cellulose by electrospinning [21], [48]. It also hinders elongation and nanofibrillation of the cellulose in the solution during the electrospinning. In addition to that, lignin specifically affected the viscosity of the cellulose solution in ionic liquid which affect its electrospinnability. Decrease in lignin content improves nanocellulose web morphology, average diameter and uniformity.

However, the presence of small amount of hemicellulose, was known to facilitate beating of pulp which relates to the phenomenon of "hornification" [18], [49]. The mechanism of hornification is described as the formation of coalesced microfibrils by irreversible hydrogen bonds. The presence of hemicellulose in the production of nanocellulose by wet disk milling has shown to be beneficial, and features such as decreased hornification and higher mechanical strength were observed. According to Iwamoto *et al.* [50], degree of nanofibrillation of wood pulp containing hemicellulose was higher compared to pure wood pulp cellulose. Hemicellulose can play the role of regulators during the association of cellulose into fibrils where it increases the porous structure of pulp fibers which resulted the decreased in diameter size of nanocellulose [51].

3.2 *Polymer composites*

Polymer composites using natural fibers are poised to see explosive development in the next few years.

Although there are many different types of thermosetting resins being used in the composite industry, the structural parts are mainly made of thermoplastic, polyester, vinylester, epoxy and phenol-formaldehyde [41], [52], [53]. The main bottlenecks in the broad use of these natural fibers in various polymer matrixes are the poor compatibility between the fibers and the matrix and the inherent high moisture absorption characteristic which brings about dimensional changes in the lignocellulosic based fibers [54].

Composites are developed with these polymers as the matrix with natural fiber as the reinforcement. The results show decreased strength and modulus with increasing the fiber volume fraction [55], [56]. This indicates ineffective stress transfer between the fiber and matrix due to lower adhesion. It is necessary to bring a hydrophobic nature to the fibers by suitable chemical treatments in order to develop composites with improved mechanical properties. The presence of too high of hemicellulose content will affect the degree of crystallinity of fiber, leading to poor mechanical properties of polymer composite obtained [61]. Besides that, the thermal and crystallinity properties of polymer composite are also influence by the chemically treated fibers. Table 3 summarizes all the importance of chemical pretreatment that influence the final properties of polymer composites.

3.3 *Biosugars*

Lignocellulosic biomass has attracted attention of researchers due to its potential utilization for biosugars. These biosugars are produced by the hydrolysis process and can be used for the production of ethanol by the fermentation process. However, the presence of hemicellulose and lignin hinders the access of the cellulase to cellulose, thus resulting in low efficiency of the hydrolysis. Previous research have shown that, by removing hemicellulose and lignin, reduction of cellulose crystallinity and increase of porosity from pretreatment processes can substantially improve the enzymatic hydrolysis. The chemical pretreatment is necessary to get rid of this recalcitrance prior to saccharification for bioethanol and biofuels production. Table 4 shows several findings on the chemical pretreatment of lignocellulosic biomass for the production of biosugars.

4 Types of Chemical Pretreatment

There are several chemical pretreatment has been explored and each pretreatment has their own specific process (Figure 3). Most of the chemical pretreatment are used to reduce the amount of hemicellulose and lignin. The effect of chemical pretreatment on the composition of several natural fibers are shown in Table 5. Some of the chemical pretreatment as discussed in this section are combine with thermal pretreatment. This is aim to reduce the use of chemicals and also to increase the effectiveness of the pretreatment.

4.1 *Weak acid hydrolysis*

One of the most effective pretreatment methods for lignocellulosic biomass is dilute acid treatment. There are two types of weak acid hydrolysis in general.

Table 3: The influence of chemical pretreatment of the properties of polymer composites

Composite	Findings	Reference
Wood fiber/ polypropylene	- The results demonstrate that treated significantly influence the fiber–matrix interfacial bond. - The composite containing fibers pretreated with an acid-silane aqueous solution exhibits the highest tensile properties among the materials studied.	[57]
Oil palm empty fruit bunch/polypropylene	- The fiber was were treated with alkaline peroxide to remove lignin. - The mechanical properties were improved. - Elimination of lignin contents of fibre strongly influenced on the properties of composite.	[58]
Hemp fiber/ polyester	- Alkaline treated fiber composite properties increased as a result of greater interface bonding. - The opposite results were achieved in the case of alkalized fiber that was further treated with acetyl and silane treatments. -Treated fibre were able to effectively improve the bonding properties of composites, even though the mechanical strength of these fibres could be decreased.	[59]
Bamboo fiber/ polylactic acid	- A synergistic treatment including dopamine (DA) modification and alkali pretreatment on bamboo fiber (BF) was used as reinforcement in a polylactic acid (PLA) matrix. - Compared with the untreated bamboo fiber/polylactic acid composites, the synergistic treatment improved the thermal properties and mechanical properties.	[60]

Table 4: Chemically treated lignocellulosic biomass for the biosugars production

Lignocellulosic Biomass	Findings	Reference
Oil palm mesocarp fiber	- The performance of HNO_3 and NaOH pretreatment on oil palm mesocarp fiber was evaluated based on the residual carbohydrate. - The pretreated fiber improved cellulose concentration from 33.14% to 60.0%, while hemicellulose, lignin and ash were reduced by 25.59, 10.0 and 25.9% to 10.0, 5.33 and 3.0%, respectively. - Enzymatic treatment using 1g solid loading, produce highest production of biosugars.	[62]
Miscanthus sacchariflorus	- The effect on combination of fiber pretreatment with continuous alkaline single-screw extrusion and ultrasonication towards biosugars production was evaluated. - The results show that ultrasonication with continuous alkaline pretreatment increased the enzymatic digestibility of carbohydrates and reduced the use of chemicals during pretreatment. - The developed method can be considered an effective and eco-friendly approach to the production of bio-based materials.	[63]
Sugarcane bagasse pith	- The fiber was pretreated with different sulfuric acid. - The pretreated solid was hydrolyzed using a commercial enzyme (Celluclast® 1.5 L). - The maximum total sugars yield (67%) of total sugars in the treated bagasse pith.	[64]

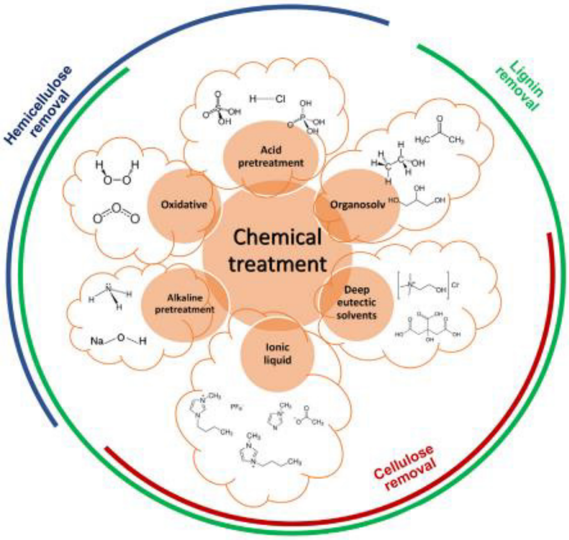

Figure 3: Graphical diagram of various chemical pretreatment methods. Image adapted from [65].

a) A high-temperature, continuous-flow process for low-solids loading (T > 160°C, 5–10 wt% substrate concentration).

b) High-solids loading at low temperatures and in batches (T ≤ 160°C, 10–40% substrate concentration).

The raw material is sprayed with dilute (mostly sulphuric acid, H_2SO_4), and the mixture is held at 160–220°C for short periods up to a few min. The hemicellulose then undergoes hydrolysis, releasing monomeric sugars and soluble oligomers from the cell wall matrix into the hydrolysate. Hemicellulose removal increases porosity and improves enzymatic digestibility, with complete hemicellulose removal usually resulting in maximum enzymatic digestibility [66]. Organic acids (e.g., maleic acid, fumaric acid) can be used instead of inorganic acids for dilute acid pretreatment [67].

The treatment performs well in terms of recovering hemicellulose sugars, but it has some drawbacks. The hemicellulose sugars could be degraded further to furfural and hydroxymethyl furfural (HMF), both of which are strong inhibitors of microbial fermentation. Furthermore, acids can be corrosive, and neutralization produces solid waste. The treatment offers good performance in terms of recovering hemicellulose sugars but there are also some drawbacks. The hemicellulose sugars might be further degraded to furfural and HMF, strong inhibitors to microbial fermentation. Furthermore, acids can be corrosive and neutralization results in the formation of solid waste. The method is especially suitable for biomass with low lignin content, as almost no lignin is removed from the biomass [68].

Hernandez *et al.* [69] used dilute H_2SO_4 (1 g per 100 g of reaction mixture) pre-hydrolysis as a pretreatment for the enzymatic hydrolysis of cellulose from Moringa oleifera residual empty pods. The cellulose recovery in pretreated solids was obtained at a temperature of 130°C and a pressure of 1 bar. The reaction time after 10 min was greater than 90%. With a temperature of 190°C and a reaction time of 30 min, the cellulose recovery rate dropped to 81–85%, which can be attributed to partial solubilization of the easily hydrolyzed fraction. During the pretreatment at 160°C for 20 min, the highest sugar concentration in the acid hydrolysates and the highest conversion (84.3%) of

Table 5: Chemical composition of nanofibers of various sources before and after chemical treatments

Lignocellulosic Biomass	**Composition**			**References**
	Cellulose	**Hemicellulose**	**Lignin**	
Oil palm empty fruit bunch				[31]
Untreated	40 ± 2	23 ± 2	21 ± 1	
Treated	90 ± 1	4 ± 1	2 ± 0.1	
Rubberwood				[31]
Untreated	45 ± 3	20 ± 2	29 ± 2	
Treated	91 ± 1	5 ± 1	4 ± 1	
Pineapple leaf				[31]
Untreated	81.3 ± 2.4	12.3 ± 1.3	3.5 ± 0.6	
Treated	98.6 ± 0.5	0.5 ± 0.0	0.8 ±0.4	
Bamboo (stem)				[32]
Untreated	46.4 ± 4.3	27.1 ± 3.3	25.0 ± 2.2	
Treated	80.2 ± 4.2	17.7 ± 3.3	1.1 ± 0.3	
Wood (Needle fir)				[32]
Untreated	46.4 ± 4.3	27.1 ± 3.3	25 ± 2.2	
Treated	80.2 ± 4.2	17.7 ± 3.3	1.1 ± 0.3	
Flax (bast)				[33]
Untreated	73 ± 3	13 ± 2	5 ± 1	
Treated	95 ± 1	1 ± 1	3 ± 1	
Flax (stem)				[32]
Untreated	75.4 ± 0.2	13.4 ± 2.8	3.4 ± 0.9	
Treated	88.8 ± 1.5	9.1 ± 1	0.4 ± 0.1	
Wheat straw				[32]
Untreated	43.2 ± 0.15	34.1 ± 1.2	22.0 ± 3.1	
Treated	84.6 ± 4.41	13.9 ± 2.1	9.4 ± 0.8	
Wheat straw (stem)				[32]
Untreated	39.8 ± 3.1	34.2 ± 2.7	19.8 ± 2.6	
Treated	84.1 ± 2.6	13.9 ± 2.1	1.9 ± 0.3	
Soy hulls				[33]
Untreated	56.4 ± 0.92	12.5 ± 0.72	18.0 ± 2.5	
Treated	94.0 ± 1.53	3.5 ± 0.8	2.5 ± 0.4	
Kenaf (bast)				[34]
Untreated	63.5 ± 0.5	17.6 ± 1.4	12.7 ± 1.5	
Treated	92 ± 1.4	5.2 ± 0.6	0.5 ± 0.4	
Kenaf (stem)				[31]
Untreated	58.0 ± 1.0	22.0 ± 1.0	17.5 ± 1.3	
Treated	91.00 ± 1.0	6.0 ± 1.8	1.0 ± 0	

cellulose in the enzymatic hydrolysis were obtained. The furfural concentration reached 4.04 g/L after 20 min at 160°C and decreased as the temperature and reaction time increased. Only in the highest temperature were HMF, formic and levulinic acids formed.

4.2 *Strong acid hydrolysis*

Concentrated strong acids, such as H_2SO_4 and HCl, have been widely used to treat lignocellulosic materials because they are powerful cellulose hydrolysis agents, and no enzymes are required after the acid hydrolysis [70]. The flexibility in feedstock selection, high monomeric sugar yield, and required mild temperature conditions are all advantages of concentrated acid hydrolysis. The disadvantages of using concentrated acids are the corrosive nature of the reaction and the need to recycle acids to reduce costs. Several companies are currently working to commercialize strong acid hydrolysis of lignocellulosic biomass for microbial fermentation.

Hafid *et al.* [71] extracted cellulose from rice husk (RH) using concentrated HNO_3. More than 65.51% of cellulose was recovered with low residual hemicellulose and lignin content. Moreover, acid hydrolysis by HNO_3 resulted in a 2.01–fold increase in cellulose content and some improvement in cellulose crystallinity up to 40.8%. The treated RH had turned into a white powder, and the extracted solution had become light yellow due to initial decomposition of monosaccharides into smaller molecular sizes, such as sugar mixtures and product dehydration, such as furfural and HMF.

4.3 *Alkaline hydrolysis*

The removal of lignin from the biomass is the primary effect of alkaline pretreatment, which improves the reactivity of the remaining polysaccharides. Consequently, alkali pretreatment remove acetyl and the various uronic acid substitutions on hemicellulose, which reduces the enzyme's accessibility to the hemicellulose and cellulose surfaces. According to reports, the mechanism of alkaline hydrolysis is based on the saponification of intermolecular ester bonds that crosslink xylan, hemicelluloses and other components such as lignin [70].

Gundupalli *et al.* [72] aim to reduce waste accumulation by using sodium hydroxide to extract lignin and sugar from accumulated pith. Pith was utilized as a substrate for the recovery of Kraft lignin (KL) and sugar, as it contains roughly 24% cellulose and 49% lignin. With an ideal biomass loading of 65 mg/mL, a NaOH concentration of 5.12% w/w, a residence duration of 31 minutes, and a temperature of 121°C, maximum KL recovery up to 86% was obtained. After 48 h of saccharification, a 95% glucose yield was produced.

4.3.1 Calcium or sodium hydroxide

Sodium hydroxide or lime (calcium hydroxide) are commonly used. Salts are formed as a result of the use of these components and must be removed or recycled if they are to be incorporated into the biomass [73], [74]. Although the process conditions are relatively mild, reaction times can be lengthy. These mild conditions prevent lignin condensation, resulting in high lignin solubility, particularly for low-lignin biomass such as softwood and grasses. Sugar degradation to furfural, HMF, and organic acids is limited due to the mild conditions. The addition of air or oxygen to the reaction mixture improves delignification significantly, especially for highly lignified materials [75].

Jiang and co-researchers have investigated the comparison between sodium hydroxide and calcium hydroxide pretreatment of giant reed for enhanced enzymatic digestibility and methane production [76]. For improved enzymatic digestibility and biogas production from giant reed, a promising energy crop, researchers compared NaOH pretreatment with leachate reuse and $Ca(OH)_2$ pretreatment. NaOH pretreatment with leachate reuse increased glucose yields by 2.6 times during enzymatic hydrolysis and methane yields by 1.4 to 1.6 times during anaerobic digestion, respectively. However, the net benefit of NaOH pretreatment was negative (i.e., revenue from increased energy production less chemical cost). Not only did pretreatment with 7–20% $Ca(OH)_2$ increase glucose and methane yields by up to 2.3 and 1.4 times, respectively, but it also resulted in a net benefit of \$1.1–5.8 per tonne dry biomass.

4.3.2 Ammonia

At high temperatures, pretreatment with aqueous ammonia reduces lignin content and removes some hemicellulose while decrystallizing cellulose. The ammonia fibre explosion-method (AFEX), ammonia recycle percolation (ARP), and soaking in aqueous ammonia are all examples of ammonia pretreatment techniques.

In a flow-through column reactor, the biomass is pretreated with aqueous ammonia. The high-temperature liquid flows through the reactor column, which was previously packed with biomass. The reactor system must be slightly pressurized (e.g., 2.3 MPa) to prevent flash evaporation [77], [78]. Following the reaction, the liquid is separated from the solid fraction, which is rich in cellulose and hemicellulose. This liquid fraction is then passed through a steam-heated evaporator to recover ammonia and separate lignin and other sugars. The separated fraction is then sent into a crystallizer, while the ammonia is recycled to the reactor inlet. Following crystallization, a washing step is performed to extract the sugars that have been retained in the solid matrix.

By minimizing the interaction with hemicellulose, soaking in aqueous ammonia (SAA) at a low temperature efficiently removes lignin from the raw material. As a result, the surface area and pore size are increased. Most commercial xylanase and cellulase mixtures can hydrolyze retained hemicellulose and cellulose to fermentable sugars. SAA was tested as a biomass pretreatment method by Kim *et al.* [77]. Destarched barley hull was treated with 15-30% aqueous ammonia at 30–75ºC for 12 h to 77 days with no agitation and a solid-to-liquid ratio of 1:12 in their study. After soaking, the solids were filtered, washed, and analyzed. As a result of treating biomass with 15% aqueous ammonia at 75ºC for 48 h, they obtained 66% lignin solubilization and observed saccharification yields of 83% for glucan and 63% for xylan. The cost of ammonia, particularly ammonia recovery, determines the cost of pre-treatment [79]. However, total sugar yields achieved have a significant impact on biomass pretreatment economics.

Kim and co-workers have investigated the pretreatment of corn stover by aqueous ammonia [78]. In a flow-through column reactor, corn stover was pretreated with aqueous ammonia, a process known as ammonia recycled percolation (ARP). This method was extremely effective at delignifying biomass, reducing the lignin content by 70–85%. The majority of the lignin was removed within the first 20 min of the process. The removal of lignin by ARP was confirmed further by FTIR analysis and lignin staining. The ARP process dissolved 40–60% of the hemicellulose while leaving the cellulose intact. The oligomeric form of the solubilized carbohydrate existed. Carbohydrate decomposition was minimal during the pretreatment. Corn stover treated for 90 min had 99% enzymatic digestibility, with 60 FPU/g of glucan. Enzymatic digestibility of corn stover treated for 90 min was 99% with 60 FPU/g of glucan enzyme loading and 92.5% with 10 FPU/g of glucan. ARP-treated corn stover digestibility was significantly higher than that of -cellulose. The removal of lignin and hemicellulose was related to enzymatic digestibility, possibly due to increased surface area and porosity. The SEM images revealed that the pretreatment had deformed the biomass structure and exposed its fibers. The crystallinity index increased with pretreatment, indicating that the amorphous portion of the biomass was removed.

4.4 *Organosolv*

Organosolv processes remove lignin with an organic solvent or mixtures of organic solvents and water prior to enzymatic hydrolysis of the cellulose fraction. In addition to lignin, cellulose fraction and hemicellulose syrup of C5 and C6 sugars are produced during the organosolv pretreatment process. The removal of lignin from biomass exposes the cellulose fibers to enzymatic hydrolysis, resulting in higher biomass conversion [80]. Ethanol, methanol, acetone, and ethylene glycol are common solvents used in the process. Temperatures used in the process can reach 200°C, but lower temperatures may be sufficient depending on factors such as the type of biomass used and the use of a catalyst. Inorganic or organic acids are examples of possible catalysts [70].

The solvent itself may act as an inhibitor of enzymatic hydrolysis and fermentation. As a result, prior to fermentation, the solvent must be (partially) removed. The solvent must be removed and recovered in order to reduce its cost and environmental impact.

The following are some of the advantages of organosolv pretreatment:

- Production of a high-quality lignin that could allow higher-value lignin applications such as (platform) chemical production.
- Separation of lignin prior to enzymatic hydrolysis of the cellulose fraction could potentially lower enzyme costs. In addition to improved cellulose fiber accessibility, the absorption of cellulase enzymes to lignin is reduced by removing lignin beforehand.

The following are the disadvantages of organosolv pretreatment:

- The high cost of the solvents, which can be mitigated by recovering and recycling solvents via evaporation and condensation. Solvent removal is critical because solvents can have a negative impact on microorganism growth, enzymatic hydrolysis, and fermentation [80].
- The high risk of handling harsh organic solvents that are highly flammable. It can cause severe damage and large fire explosions in the absence of proper safety measures.

Park *et al.* [81] investigated the effect of various catalysts (H_2SO_4, NaOH, and $MgSO_4$) on pine and discovered that H_2SO_4 was the most effective in terms of ethanol yield. However, when the concentration of NaOH was increased by 2%, it was found to be effective in terms of digestibility. H_2SO_4 has a high reactivity and thus has proven to be a very strong catalyst; however, it is toxic, corrosive, and inhibitory in nature.

4.5 *Oxidative delignification*

Lignocellulosic biomass can also be delignified by using an oxidizing agent such as hydrogen peroxide, ozone, oxygen, or air. The high reactivity of oxidizing chemicals with the aromatic ring, as discussed earlier in the document, accounts for the effectiveness in delignification. As a result, the lignin polymer will be converted into, for example, carboxylic acids. Because the acids formed will act as inhibitors during the fermentation process, they must be neutralized or removed. Oxidative treatment affects the hemicellulose fraction of the lignocellulosic biomass in addition to lignin. A significant portion of the hemicellulose may have degraded and is no longer usable for sugar production.

Hernández-Guzmán *et al.* [82] compare an alkaline oxidative pretreatment of wheat straw carried out in a stirred tank reactor using a semi-batch and a conventional operation. The efficiency of the treatments was determined by analyzing the lignocellulosic content of the biomass and enzymatic hydrolysis of pretreated biomass utilizing the Cellic® CTec2 enzyme complex by Novozymes®. Semi-batch operation requires less time than batch operation and allows for a bigger load of biomass, with a delignification yield of 55–60%. When employing the mesh #>60 mesh and #40–60 mesh, respectively, the enzymatic hydrolysis studies obtained their highest yields of 72 and 66% according to reducing sugars conversion in the first 5 h of reaction time.

4.5.1 Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a common oxidative compound. In a solution of 2% H_2O_2 at 30°C, approximately 50% of the lignin and the most of the hemicellulose was dissolved. Enzymatic hydrolysis yields can reach up to 95% [83]. H_2O_2 allows biomass fractionation at ambient pressures and low temperatures, allowing low-cost reactors being used.

Ali *et al.* [84] studied the influence of pretreatment of bamboo culms with alkaline hydrogen peroxide (AHP), structural alterations, and enzymatic hydrolysis The findings revealed that cellulose component increased by 36.87%, hemicellulose reduced by 50.66%, and lignin increased by 37.94% in contrast to the chemical components in the raw material. After AHP treatment, dried bamboo residues yielded approximately 370 mg reducing sugars per gram.

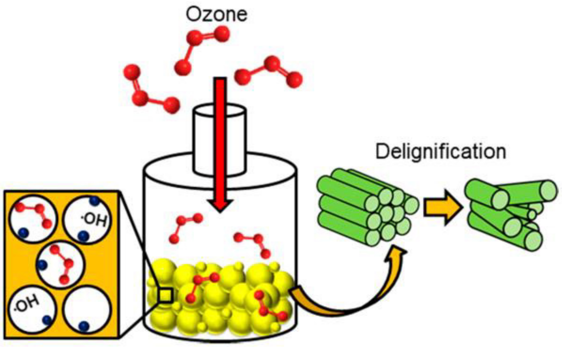

Figure 4: Schematic diagram of ozonolysis process and its impact on delignification and the generation of hydroxyl radicals in the porous network of biomass waste particles (yellow color = biomass particle, black color = water molecules). Image adapted from ref. [85].

4.5.2 Ozonolysis

Ozone treatment is primarily used to reduce lignin content in lignocellulosic biomass because it primarily degrades lignin while having little effect on hemicellulose and cellulose [12]. By attacking and cleaving aromatic rings structures, ozone treatment focuses on lignin degradation, while hemicellulose and cellulose are barely decomposed (Figure 4). Many different lignocellulosic materials, such as wheat straw, bagasse, pine, peanut, cotton straw, and poplar sawdust, can be used to disrupt their structure [70], [86], [87]. Vidal and Molinier designed and developed a laboratory-scale ozonolysis setup for the pretreatment of various biomasses [88].

Wheat straw pretreatment in the aforementioned reactor resulted in lignin removal of 60% and a fivefold increase in enzymatic hydrolysis. The percentage of lignin in poplar sawdust was reduced to 8%, while sugar yield increased to 57% [88]. Ozonolysis, unlike other chemical pretreatment methods, is carried out at room temperature and pressure. It also produces no toxic inhibitors, making it environmentally friendly and unaffected by post-treatment processes such as enzymatic hydrolysis and yeast fermentations [89]. The moisture content of the biomass has a significant impact on ozone pretreatment; the higher the moisture content, the lower the lignin oxidation. Although ozonolysis is an effective pretreatment method, the large amount of ozone required makes it an expensive pretreatment method, making it unsuitable for industrial scale pretreatment.

To develop an economically viable pretreatment method, research is being conducted in a variety of areas, including the generation of industrially feasible ozone concentrations, the development of reactors such as packed bed, fixed-bed, and stirred tank semi-batch reactors capable of accommodating large quantities of low moisture (< 30%) biomass residues with particle sizes ranging from 1 and 200 mm.

Sugarcane straw residue (SCS) was used by Ortega *et al.* [90] to produce fermentable sugars. SCS was treated with a combination of impregnation in various medium and ozonolysis. The basic medium (80°C at atmospheric pressure for 8 h) produced significant results, followed by ozonolysis (rotary reactor, 0.24% w/w ozone concentration, 60 min reaction time, and % moisture content). The quantity of glucose released did not increase when the ozone concentration was increased from 0.24% to 1.3% (w/w) (yields of 60.8 and 60.2%, respectively), demonstrating that high ozone concentrations are not necessary. Contrarily, cellulose and hemicellulose content increased by 75% and 42%, respectively, while the lignin content reduced by 47% as compared to the raw material. Furthermore, samples exposed to ozonolysis demonstrated the highest reduction in recalcitrance to enzymatic hydrolysis, yielding 60 and 71% of glucose and xylose conversion, respectively when compared to impregnated material (26 and 31% respectively) and raw material (4 and 5%).

4.6 *Room Temperature Ionic Liquids (RTIL)*

Room Temperature Ionic Liquids (RTIL) are salts that are liquid at room temperature. There are many different types of RTIL, but they all have one thing in common: they are usually made up of an inorganic anion and an organic cation with a very heterogeneous molecular structure. Because of the difference in molecular structure, the ion bonding is weak enough for the salt to appear liquid at room temperature [91].

Ninomiya and co-researchers proposed an ionic liquid pretreatment method for lignocellulose nanofibers (LCNFs) preparation [92]. In this study, bagasse powder was treated with choline acetate as an ionic liquid, and LCNFs were obtained through mechanical nanofibrillation. Ionic liquids, on the other hand, are expensive, which will impede the scaling application for the preparation of CNFs. Li *et al.* [93] also successfully prepared CNFs using 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to treat sugarcane bagasse followed by high pressure homogenization.

RTIL has yet to be used in an industrial application. Furthermore, there is very little information in the literature to describe their interaction with lignocellulosic biomass [94]. However, there is evidence that they can function as selective lignin or cellulose solvents, owing to their polarity and unique properties in general. Under ambient conditions and without the use of an acid or alkaline solution, this would result in lignin separation and increased cellulose accessibility. Inhibitor compound formation could also be avoided.

Despite the potential of this method, there are several uncertainties due to a lack of experience. The ability to recover the RTIL used, the toxicity of the compounds, and the combination of water and RTIL are among the most important.

5 Conclusions

Growing interest in the use of lignocellulosic biomass has been highlighted by a spike in the number of research in this area. Given the diversity of lignocellulosic materials, developing a general process design for all raw materials seems difficult. Therefore, defining “The optimal pretreatment approach” remains challenging. Pretreatment of lignocellulosic biomass has included biological, mechanical, and chemical methods as well as multiple combinations of these. Chemical pretreatment of biomass has shown to be one of the most promising approaches for optimizing the utilization of these materials to produce bioproducts. Throughout the end, anything relies on the proposed application, and any recommendation must be based on a detailed techno-economic research, including data obtained from at least a pilot scale. The final application plays a significant role in deciding which chemical pretreatment approach to use.

Chemical pretreatment as discussed in this review could prove to be an ideally suitable process for conversion of lignocellulosic biomass, including agricultural and forestry residues for several important bioproducts.

In addition, diverse advantages have also been reported for most of the pretreatment methods, which make them interesting for industrial applications. Although, pretreatment systems and the concomitant release of bioproducts from lignocellulosic biomass have been greatly improved by new technologies, there are still challenges that need to be further investigated. Some of these chemical pretreatment have disadvantages such as high cost as well as an environmental concern due to large amounts of chemical residues that require safe handling and disposal after the pretreatment. It is not possible to define the best pretreatment method as it depends on many factors such as type of lignocellulosic biomass, process parameters, environmental impact, and economical feasibility.

Combination thermal and chemical pretreatment techniques have received a lot of attention in recent years to overcome this disadvantage as well as to reduce energy consumption during thermal pretreatment methods. However, research in this area is still limited. Therefore, extensive research can be focused in this area. Besides that, enhancement of production based on economies of scale for more efficient and cost-effective conversions to value-added products for every chemical pretreatment should be given.

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