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Updates on the pretreatment of lignocellulosic feedstocks for bioenergy production- a review

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Abstract

Lignocellulosic biomass is the most abundant renewable energy bioresources available today. Due to its recalcitrant structure, lignocellulosic feedstocks cannot be directly converted into fermentable sugars. Thus, an additional step known as the pretreatment is needed for efficient enzyme hydrolysis for the release of sugars. Various pretreatment technologies have been developed and examined for different biomass feedstocks. One of the major concerns of pretreatments is the degradation of sugars and formation of inhibitors during pretreatment. The inhibitor formation affects in following steps after pretreatments such as enzymatic hydrolysis and fermentation for the release of different bioenergy products. The sugar degradation and formation of inhibitors depend on the types and conditions of pretreatment, and types of biomass. This review covers the structure of lignocellulose, followed by the factors affecting pretreatment and challenges of pretreatment. This review further discusses diverse types of pretreatment technologies and different applications of pretreatment for producing biogas, biohydrogen, ethanol and butanol.

Keywords: Lignocellulosic biomass, pretreatment, biogas, ethanol, butanol, inhibitors

1 Introduction

Lignocellulosic biomass is composed primarily of cellulose, hemicellulose, and lignin. Cellulose is a homogenous polymer composed of glucose (six carbon sugars), however, hemicellulose is a heteropolymer predominantly composed of five carbon sugar sub-units such as xylose, mannose, and arabinose. However, the composition of different compounds in the hemicellulose varies for the type of biomass. The hemicellulose makes side chain connections between the cellulose and lignin portions. Lignin is a complex aromatic polymer that covers the sugar polymer matrix to serve as a protective barrier from physical and chemical attacks. Some of the most common examples of lignocellulosic biomass include energy crops, forest/wood residues, agri-residues, pulp and paper wastes and municipal solid waste, etc. [1]. Lignocellulosic biomass is the most abundant bioresource with the availability of nearly 200 billion metric dry tons annually [2]. Typically, lignocellulose is comprised of 30-70% carbohydrates (cellulose and hemicellulose, collectively known as holocellulose) which are a potential source for the production of bioenergy and biobased products [3]. Apart from celluloses and hemicelluloses, lignin the third major component is the lignocelluloses is also a source for energy/biobased products such as electricity, resins, and flavor compounds [4].

The complexity of lignocellulosic feedstocks leads to the difficulty to release the fermentable sugars, which are the precursors to produce a plethora of bioenergy and biobased products [5]. The complex structure of the plant protects it against microbial and enzymatic attacks which are known as biomass recalcitrance [6]. Plants provide protection in many ways: the outer layer or epidermis contains thick-walled cells, which produce waxes or oily substances. Such substances make the plant resilient to different physical and chemical attacks. The inner layer of the epidermis consists of vascular tissues and cell walls [7]. Polymers such as hemicelluloses, lignin, and pectin surround

cellulose microfibrils in the plant cell walls. The main reason behind such a recalcitrant nature of lignocelluloses is associated with strong interaction among cellulose, hemicellulose, and lignin [8]. This interaction poses a challenge for the utilization of biomass structural sugars. To access the holocellulose component of the biomass, pretreatment is required to boost the release of monomeric sugars [9]. Pretreatment can dramatically enhance enzymatic hydrolysis of lignocellulosic biomass thereby facilitating efficient sugar release for subsequent transformation to biofuels and biobased products, but it is also one of the most costly steps in the bioconversion process, accounting for around 20% of the total cost of the plant [10]. Although it is costly, there are numerous advancements that have taken place in pretreatment technologies that aim to help lower the cost of pretreatment [11]. A large variety of pretreatment strategies exists for lignocellulosic biomass, which is designed to remove or alter lignin, hemicellulose, and/or cellulose structures, and increase the susceptibility of these components to enzymatic attack or removal. The four major categories of pretreatment are: physical, chemical, biological and hybrid. Physical pretreatments usually reduce the particle size and in turn increase the surface area, thus improving the efficiency of other possible downstream pretreatments. Chemical pretreatments utilize acids or bases to target the removal of specific biomass structural components via chemical reactions. Biological pretreatments use microorganisms (typically fungi) to alter and remove components of the lignocellulosic structure by producing enzymes which degrade the biomass structure. Hybrid pretreatment combines traits of two or more other pretreatment methods to maximize the positive effects of both pretreatments and maximize sugar release following enzyme hydrolysis.

It is important to understand the complex biochemistry and structure of biomass for effective pretreatment. This review attempts to focus on the structure of lignocellulose, followed by the different pretreatment technologies. Furthermore, a brief discussion on inhibitor formation during

different pretreatments as well as various pretreatments and its effects on applications including biogas, ethanol, and butanol production are also presented.

2 Lignocellulosic biomass

Lignocelluloses comprises of three major components including celluloses, hemicelluloses, and lignin. Table 1 shows the composition of this three different components for various lignocellulosic biomass [12]. Cellulose comprises a linear chain of β-1,4 linked d-glucose units, whereas hemicelluloses are heteropolymers including xylan, mannan, galactan, arabinan, etc. which are linked by 1,4 glycosidic bonds [13, 14]. Lignin, on the other hand, is formed from the oxidative coupling of three alcohols groups including *p*-hydroxycinnamoyl, coniferyl and sinapyl alcohols. The composition of these different components and their proportion vary depends on the biomass, the part of the plant material and at what time it was harvested or cultivated, which is why a unified pretreatment technique couldn't be used for all the biomass [14]. For instance, softwoods contain a higher fraction of mannose as a part of hemicelluloses, whereas hardwoods contain more lignin and heterogeneous hemicelluloses. Softwoods usually comes from conifer which are usually evergreen, while hardwoods arise from deciduous tree which loses its leaves annually. Softwood are less dense in comparisons with hardwood since they are slower growing. In addition, softwoods are easier to cut as it is less dense, in contrary to hardwoods which are sturdier [15].

2.1 Anatomy

The plant cell wall is complex and has many distinct functions including absorption of nutrients, secretion, protection, food reserve, cell shape maintenance, and control of cell expansion. Furthermore, the intracellular spaces provide mechanical strength. When the cell wall divides, two

walls are formed from the pre-existing wall. These are called as primary cell walls. Nonetheless in some cells, for instance, fiber cells in woods, an additional cell wall is formed after primary cell division, which is known as secondary cell walls. Generally, secondary cell walls are located inside the primary cell walls. Primary cell walls are usually not lignified, whereas the secondary cell walls are highly lignified [16, 17].

The plant cell wall contains microfibrils that are interconnected by hemicelluloses. Pectin and lignin fill the space between microfibrils and hemicelluloses. One cell is connected to another by middle lamellae, a lignin-rich outer layer of the cell wall. Cellulosic microfibrils that are arranged randomly represent the outer layer (the primary cell wall). The secondary cell wall is distinguished into three sub-layers, namely outer (S1), middle (S2), and inner (S3) layers. Figure 1 shows the different layers of the cell wall. The thickness of each layer differs but the S2 layer is generally the thickest. In the S1 layer, microfibrils are arranged horizontally, whereas, in the S2 layer, they are vertically aligned. Finally, the S3 layer is again arranged horizontally [18, 19]. The tough mechanical and physical properties of the cell wall are mainly due to the vertical orientation of the cell wall. Sometimes in some cells, for instance, stem tissues of barley straw, an additional cell wall called a tertiary wall (T) covering the secondary wall is present. The cellulosic microfibrils are arranged randomly in the tertiary wall, unlike the primary and secondary wall [18, 20].

2.2 Recalcitrance

The cellulose present in plant cell walls is synthesized in the plasma membrane, whereas hemicellulose is synthesized and secreted from Golgi apparatus [16]. A cellulose microfibril contains 36 hydrogen-bonded cellulose chains arranged parallel to one another. Nevertheless, recent studies showed that the hydrogen bonds could be greater than 36, suggesting that the

previous investigations could be an approximation [21]. The synthesis of microfibrils in the plant cell walls is enhanced by an enzyme known as cellulose synthase, which possesses an active site catalyzing glucan polymerization resulting in aggregation of microfibrils [22].

Morphology of cellulose

Cellulose is polymorphic and hence it can transform into different crystalline forms, namely cellulose I, II, III, and IV [23]. In nature, cellulose I am formed involving two crystal phases, i.e., monoclinic (I_β) and triclinic (I_α). Monoclinic cellulose is arranged into two parallel chains in the upward direction and packed as sheets. Conversely, the triclinic structure contains a single chain. The glycosyl linkage and hydroxymethyl groups are common for both monoclinic and triclinic cellulose. Even though monoclinic cellulose possesses high crystallinity, the intermolecular hydrogen bonds maintain the cellulosic chains as sheets [24].

The monoclinic and the triclinic celluloses interact without bonding when they are packed onto each other. There is a possibility for three types of interactions: (1) intra-chain O–H–O bonds between glucose residues of the same chain and sheet; (2) inter-chain O–H–O bonds between glucose residues of the same sheet but different chains; and (3) inter-sheet C–H–O bonds in terms of van der Waals interactions between neighboring sheets. These complex interactions result in the high resistance of cellulose towards different attacks [25]. Monoclinic is more stable compared to triclinic structures, which is due to the absence of two additional inter-sheet hydrogen bonds in triclinic structures. Heating at temperatures higher than 260°C could transform the less stable triclinic to monoclinic structures. Nonetheless, in nature monoclinic is more abundant than triclinic cellulose [25].

The other allomorph of cellulose, i.e., cellulose II is formed from cellulose I by two ways: (1) dissolution of cellulose I in cellulose solvent followed by precipitation, (2) swelling cellulose I fibers using alkalis. Cellulose II contains antiparallel chains and it is monoclinic. Cellulose III is acquired from cellulose I and II by liquid ammonia treatment. Consequently, cellulose IV is obtained from cellulose III by heating [23].

Twisting microfibrils

Cellulosic microfibrils and nanofibrils are twisted in their native state and were confirmed with evidence from a microscopic study by Hanley, Revol, Godbout and Gray [26]. In the case of higher plants, the long helical twist is observed in the microfibrils. The distance between each twist depends on the dimension of microfibrils. An increase in the dimension increases the resistance of the microfibril towards forming a helix. This could be the reason for the load-bearing ability of the plants to have small dimensions [26]. It is estimated that the cellulose chains are hydrated at the fundamental level and that cellulose processing at elevated temperature reduces the hydration. So, a rise in temperature changes the state of aggregation of native celluloses. Water helps in relative motion, while removal of it causes dryness and enhances hydrogen bond formation. Cellulose dehydration by both means i.e., drying or increasing the temperature results in the tight aggregate formation and more recalcitrant native cellulose [7].

2.3 Pretreatment classifications

Pretreatment aims to enhance the accessibility of cellulose to enzymes. During pretreatment one or more of the following are achieved: (1) dissolve hemicellulose and/or lignin; (2) modify the lignin structure; (3) disrupt the matrix structure of the feedstock to reduce particle size thereby increasing the surface area; (4) reduce the crystalline structure of cellulose; or (5) pre-hydrolyze cellulose to reduce the degree of cellulose polymerization. Following pretreatment,

cellulose/hemicellulose becomes exposed and more accessible to enzymes, cellulases/hemicellulases (Figure 2a). The resulting pretreated biomass is then effectively hydrolyzed by enzymes, cellulases into glucose (Figure 2 b).

Different pretreatment methods have been developed in the past decades; however, it is still the second most expensive process on an industrial scale [27]. Some of the important factors that need to be considered while selecting the pretreatment method are high yield of readily digestible cellulose substrate, sequential fractionation of biomass, high overall sugar recovery, generation of lignin for coproducts, low capital and operating costs, low energy consumption, minimal formation of inhibitors, applicability to different types of feedstock, elimination of the need for extensive size reduction (an energy- and cost-intensive operation), and good scalability [28]. Using lignin for fuel isn't economically viable option as using it in boiler yields a price of $0.18/kg, however technical lignin's could be sold at a price of $1.08/kg. There are different forms of technical lignin including kraft, soda, organosolv, hydrolysis lignin and lignosulphonates. Sulfur-free lignin is more valuable than sulfur-rich-lignin. [29]. In the following section classification of different pretreatment methods for lignocellulosic biomass is summarized. Broadly, the pretreatment methods can be classified into physical, thermochemical, biological and other methods as elucidated in Table 2.

2.3.1 Physical methods

Physical or mechanical pretreatment aims to reduce particle size and crystallinity, which in turn increases the accessible surface area and decreases the degree of polymerization. It does not disrupt the cell walls, nor does it significantly change the structure of cellulose, hemicellulose or lignin. Physical pretreatment generally improves hydrolysis due to increased surface area, and better heat and mass transfer. All pretreatment methods require some form of mechanical

pretreatment and the size of particle used for the pretreatment process helps in efficient release of sugars. A study on milled corn for AFEX pretreatment reported that the larger particle size (>850 microns) were found to be more recalcitrant during pretreatment and hydrolysis compared with medium or smaller particle size (<500 microns) [30]. One major demerit of physical pretreatment is its energy cost. Woody feedstocks usually consume more energy for size reduction than herbaceous feedstocks. For example, energy consumptions for corn stover and switchgrass are 11.0 and 27.6 kWh/metric ton, respectively, while those for poplar and pine chips are 85.4 and 118.5 kWh/metric ton, respectively [28]. Physical pretreatment alone may not be effective for complete hydrolysis of biomass and is often combined with thermochemical pretreatments. Different physical pretreatment methods include milling and grinding.

Milling alters the ultrastructure of lignocellulose, which helps enhance the accessibility of enzyme, cellulases to the cellulose component of the structure. Milling is not only applied prior to enzymatic hydrolysis but also before other pretreatment methods such as chemical or physicochemical methods [1]. Milling is distinguished as either dry or wet milling and is selected depending on the type of biomass used. Extruders, roller mills, cryogenic mills, and hammer mills are commonly used for dry biomass such as Napier grass and corn stover. Similarly, for wet biomass such as Energy cane, wheat bran or wheat straw, colloid mill, fibrillator, and dissolver are appropriate. Ball mills are used for dry and wet processes however they are energy intensive [31]. The advantages of milling include increased hydrolysis rate, no inhibitor formation, which usually increases the overall yield for bioenergy production. Milling also has some disadvantages - it is energy intensive, and lacks the ability to remove or modify lignin [32].

Other physical methods for pretreatment of lignocellulosic biomass are high-pressure steam extrusion, pyrolysis, and electrical pulses [33]. Extrusion is a combination of heating, shearing,

and mixing through which lignocellulosic biomass is modified physically as well as chemically. A Recent advance in physical pretreatment method includes the exploration of combining enzymatic hydrolysis with extrusion [34]. Pyrolysis may also be employed for pretreatment of lignocelluloses. In pyrolysis pretreatment, lignocellulosic biomass is treated up to 300°C, and when followed by dilute acid hydrolysis, this pretreatment yields 80–85% sugars [35]. The high-pressure steam pretreatment method utilizes saturated steam at a pressure of 6-34 bars that lasts for several seconds to a few minutes. This pretreatment method results in dissolution of hemicellulose into the liquid phase, which is further decomposed into oligomeric and monomeric sugars. Now, cellulose present in the solid phase becomes easily accessible for enzymatic hydrolysis. Further hydrolysis occurs when sulfuric acid or sulfur dioxide is used as catalysts, which improves solubilization of hemicellulose [36].

Irradiation is another physical pretreatment method, which is performed using gamma radiations, ultrasound, electron beam and microwaves [37]. Irradiation improves the enzymatic hydrolysis of biomass to release sugars. In irradiation, the cellulose fraction in the lignocellulosic biomass is broken down to fibers, low molecular oligosaccharides, or even to cellobiose. Irradiation leads to dissociation of glycosidic bonds of cellulose resulting in low molecular compounds [38]. Some of the disadvantages with irradiation technique are inadequate removal of lignin, issue with the scaling up and cost [39].

In ultrasound pretreatment, the breakdown of lignocelluloses depends on the density and intensity of the ultrasonic waves. Ultrasound pretreatment generates cavitation in the liquid phase that produces significant shear force and facilitates disintegration of biomass. Ultrasound pretreatment is, however, very energy intensive. For microwave pretreatment, biomass is commonly immersed

in dilute chemical agents such as alkalis (sodium hydroxide) before it is exposed to microwaves for 5-20 minutes [27].

2.3.2 Chemical and physicochemical methods

2.3.2.1 Steam and other explosions

The explosion is a combination of physical and chemical pretreatment methods, which are performed using steam (autohydrolysis), SO_2, NH_3, or CO_2. During the explosion, the lignocellulose is heated at high pressure followed by the sudden release of the pressure. As a result of the explosion, fibers present in the lignocellulosic biomass are decompressed. Steam explosion is a popular method for pretreatment, which is usually carried out at 160–260°C and the operating time is 0.5–20 minutes [19]. For CO_2 explosion, supercritical carbon dioxide is used, as it is cheap, non-toxic, inflammable and easy to extract after the explosion. Another agent used for the explosion is ammonia, which has the advantage of high glucose yield and recovery of ammonia used, reducing the expenses [40]. The process is now widely known as ammonia fiber expansion (AFEX) to avoid the misinterpretation of term "explosion." Table 3 shows the energy consumption and its cost in terms of a functional unit (¢/L EtOH) for different lignocellulosic pretreatment adapted from Kumar et. al. [41].

2.3.2.2 Acids

Pretreatments that use acid typically use hydrochloric-, phosphoric- or sulfuric acid. This pretreatment can use high acid concentrations (30-70%) and low temperatures (below 100 °C) or low acid concentrations (0.1-10%) and high temperatures (100-250 °C). Typically, in industries, dilute acid pretreatment is preferred for economic reasons [42]. The acids used in this pretreatment method serve as a proton source to catalyze the hydrolysis reaction, which predominantly breaks apart the sugar polymers in lignocellulosic biomass. Acid pretreatment targets hemicellulose and

has a high conversion rate of decomposing and solubilizing it into monomeric pentose sugars. Studies have found that dilute acid pretreatment under the right conditions can lead to high hemicellulose recovery (85-95%) [43]. Additionally, at certain pretreatment conditions, acid pretreatment is known to remove small portions of cellulose and alter lignin structure through the removal of acid-soluble lignin [44]. Acid pretreatments are usually followed by an enzyme hydrolysis step to recover the remaining cellulose sugars. Despite the large success in removing hemicellulose and making the cellulose available for enzymatic attack, challenges associated with this pretreatment include the formation of inhibitors at harsh pretreatment conditions (high severity factor) and the need to neutralize the effluent and the remaining solids prior to downstream processing [45].

2.3.2.3 Alkali

Commonly, sodium, potassium, calcium, and ammonium hydroxides are used for alkaline pretreatment of lignocellulosic biomass. Sodium hydroxide causes swelling, which in turn increases the internal surface area and decreases the degree of polymerization. During alkali pretreatment, the intermolecular ester bonds cross-linking xylan hemicelluloses and lignin are saponified resulting in delignification. In addition, alkali pretreatment also removes acetyl groups and uronic acid from hemicelluloses. Adding oxidizing agents such as O_2 or H_2O_2 improves lignin removal [37]. Alkaline pretreatment works best for agricultural residues rather than woody biomass. Alkali pretreatment can be performed in two modes: (1) Short-term pretreatment which operates at temperatures of 100-160°C at about 13 bar pressure for few hours. (2) Long-term pretreatment which operates at lower temperatures 55-65°C up to 8 weeks at atmospheric pressure [46].

2.3.2.4 Oxidizing agents

Usual oxidizing agents used for pretreatment of lignocellulosic biomass include ozone, hydrogen peroxide, and oxygen. Oxidizing agents are generally combined with chemical and hydrothermal treatments. During ozonolysis pretreatment, degradation of aromatic and olefinic structures involves an initial electrophilic attack by oxidants. Similarly, for hydrogen peroxide, these structures are destroyed by a nucleophilic attack of hydrogen peroxide anions [37]. Ozonolysis is effective for degradation of lignin and partial degradation of hemicelluloses. Advantages of ozonolysis pretreatment include no inhibitor formation and no acids, alkali or toxic compound formation. However, ozone is expensive and there are questions with respect to scaling-up and safety. The important parameters to consider are moisture content of the sample, particle size, and concentration of the oxidizing agent. Another oxidation method, i.e., wet oxidation pretreatment involves the use of air or oxygen as an oxidizing agent. The operating temperature for this pretreatment method is generally in the range of 150–200°C with a residence time of 30 minutes. Wet oxidation breaks down hemicelluloses into monomeric sugars, lignin is oxidized and cleaved, whereas cellulose is partially degraded [35].

2.3.2.5 Organosolvs

The organic solvent or Organosolvs is another chemical pretreatment method that uses organic solvents with or without the addition of a catalyst. Organosolv pretreatment increases the accessible surface area and creates large pore volumes, results in complete removal of lignin and hemicelluloses [3, 37, 47, 48]. Table 4 shows the effect of different organic solvents as a pretreatment on various lignocellulosic biomass adapted from [49]. Standard organosolvs are alcohols, ketones, glycols, organic acids, phenols, esters, and ethers; of these, acetone is widely

used. This pretreatment method is accompanied by the addition of a catalyst such as dilute sulfuric, oxalic, salicylic, and acetylsalicylic acids, which improves the delignification rate [35, 50].

2.3.2.6 Ionic liquids

Ionic liquids (ILs) are green solvents, as they are non-toxic and non-explosive. They are salts in liquid form containing large organic cations and small inorganic anions. The roles of cations and anions are different during a pretreatment process, where cations interact with lignin by hydrogen bonding and π–π interactions. Conversely, anions act as hydrogen bond receptors, interacting with a hydroxyl group in cellulose [51]. This combination results in the efficient breakdown of lignocelluloses, which is why it is an effective pretreatment method. One of the significant advantages with ILs is the ability to recover and reuse the chemicals. Nonetheless, it is worth to mention that ILs is expensive. Some of the common ILs used in lignocellulosic pretreatment is 1-Ethyl-3-methylimidazolium acetate, 1-Allyl-3-methylimidazolium chloride, 1-Butyl-3-methylimidazolium bromide [52]. Both organosolv and IL's are distinct set of pretreatments which dissolves lignin which aren't common to other class of pretreatments.

2.4 Biological methods

Biological methods use white-, brown- and soft-rot fungi and certain bacteria for hydrolysis of lignocellulosic biomass. Fungi possess distinct characteristics associated with lignocellulosic degradation, for instance, brown- and soft-rot fungi attack cellulose and slightly modify lignin, whereas white-rot fungi target lignin predominantly [35]. Currently, white-rot fungi are being studied extensively as they specifically target lignin. Some of the commonly used white-rot fungi for biomass pretreatment for ethanol production are *Ceriporiopsis vermispora*, *Dichomitus squalens*, *Pleurotus ostreatus*, and *Coriolus versicolor* [53]. The advantages of biological pretreatments include low energy input, mild environmental conditions, and environment-friendly

[54]. The major disadvantage of the biological method is that the process is extremely slow requires few weeks to months for effective biomass hydrolysis. Thus, a large-scale application of biological pretreatment may not be an economically viable option for biofuel production [55]. Enzymatic pretreatment is another form of biological pretreatment involving enzymes from brown and white-rot fungi including laccase, manganese peroxides, versatile peroxidase, glyoxal peroxidase, and alcohol peroxidase. Enzymatic biological pretreatment is usually carried out between 35-40 °C for 6-24h [56].

Table 5 shows the effect of various pretreatment methods and their effects on different factors. Most of the pretreatments shows a high effect with respect to increasing the accessible surface area. Generating toxic compounds during pretreatment is one of the important problems which needs to be addressed. Hotwater, alkaline, oxidative and AFEX pretreatments shows a low effect when it comes to generating toxic compounds during pretreatment. Removal of lignin helps in enzyme efficiency during enzymatic hydrolysis and AFEX, lime pretreatment methods shows high effect in removing lignin during pretreatments.

3 Formation of inhibitors

During the pretreatment process, there are certain side reactions, which results in the formation of byproducts. These byproducts might be problematic for further downstream processing of pretreated biomass, such as hydrolysis, fermentation etc. due to their inhibitory attributes. Due to the recycling of processing water, the concentration of inhibitors will increase due to accumulation. Most of the inhibitors formed during the pretreatment of lignocelluloses are due to solubilization and degradation of hemicelluloses, celluloses, and lignin. Typical inhibitors formed during the

pretreatment of lignocellulosic biomass include phenolic compounds, furans, uronic acids and aliphatic carboxylic acids [57, 58].

The mechanism behind inhibitor formation is subjected to the composition of the feedstocks and types of pretreatment employed. For instance, when acid pretreatment is employed, the hemicellulose portion is degraded to pentoses and uronic acids, which is further degraded to furfural. Furfural has a boiling point of 161.7°C and though it is known to be volatile, most of the post-pretreatment processes don't happen at this high temperatures. Furfural degrades under similar conditions how it had formed. Furfural degrades to formic acid and resinous tars where it can both decompose and polymerize to form these products [59]. Similarly, hexoses are broken down to 5-hydroxymethyl-2-furaldehyde (HMF) and lignin degradation results in the formation of phenolic compounds. Acetic acid is not a direct byproduct of pretreatments because it is also formed due to hydrolysis of acetyl groups present in hemicellulose [59]. These distinct groups of inhibitory compounds affect the enzymatic hydrolysis or microbial activity.

Degradation of carbohydrates results in the formation of carboxylic acids and furan aldehydes. Formic acid and levulinic acid belong to carboxylic acids groups, while furfural and HMF are part of furan aldehydes. It is reported that concentrations of around 100 mM of acetic acid, formic acid, and levulinic acid showed an inhibitory effect on *Saccharomyces cerevisiae* using Norway Spruce [58]. For enzymatic hydrolysis, the inhibitory effects are observed when the byproducts bind to the catalytic site of cellulolytic enzymes.

Different approaches can be adopted to counteract the inhibitor formation and its negative effects. This includes feedstock selection and engineering, detoxification, bioabatement, selection of microorganisms, and use of metabolic- and evolutionary engineering approaches on the

microorganisms, among others. In feedstock selection, it is advised to use less recalcitrant substrate, which might lead to the low formation of inhibitors. For feedstock engineering, selection or engineering a plant with low recalcitrance might lead to low inhibitor formation [57]. Detoxification is a powerful technique to handle inhibitors, which are carried out by adding reducing agents, chemical additives, and polymers to convert inhibitors into less harmful compounds. Bioabatement uses microbes to remove inhibitors, however, it is a time-consuming process due to the biological nature. Designing the process to incorporate simultaneous saccharification and fermentation (SSF), etc. are other methods to overcome the inhibition issues [60]. Sometimes, microbes resistant towards inhibitors could be utilized for fermentation. Genetic engineering approaches could be employed to develop recombinant microorganisms, which are engineered towards specific inhibitors [61].

4 Pretreatment for bioenergy production

Because of pretreatment of lignocellulosic biomass, the sugars are released which are processed further into bioenergy. The type of lignocellulosic material, the method was chosen, and the demand for a product results in different bioenergy products. This section covers the various products generated from pretreatment of lignocellulosic biomass.

4.1 Biogas

For biogas production, different pretreatment methods have been suggested. For instance, liquid hot water pretreatment is beneficial, when palm fruit bunch is used as the substrate. This pretreatment resulted in an increase of 7-200% of methane yield, compared to untreated ones. The processing conditions include treating the biomass at 100-230°C for a few minutes to hours [62]. Though many pretreatment methods had positive effects, some pretreatments also showed negative

effects for biogas production, which is due to the formation of inhibitors. For example, steam-explosion and thermal acid pretreatment had a major effect on the formation of inhibitors such as furfural [9]. When lignocelluloses were treated with alkali, up to two times increase in methane yield could be achieved using agricultural residues such as wheat straw, rice straw, corn stover, beet leaves, sugarcane bagasse, and rapeseed. In general, alkali pretreatment is preferred for biomass containing large amounts of lignin [42]. More recent updates on biogas production could be obtained from [63].

4.2 Biohydrogen

Biohydrogen from lignocellulosic biomass has been widely studied and demonstrated as a feasible technology, however, pretreatment should be cost-effective to achieve this [64-66]. It is obvious that majorly raw lignocelluloses provide lower yield and production rate due to their low accessibility to for enzymes and microorganisms. Major experiments of lignocelluloses to biohydrogen were carried out using corn (stover, cob, and stalk) biomass due to its wide availability.

Cao, Ren, Wang, Lee, Guo, Liu, Feng and Zhao [67] reported the biohydrogen production from sulfuric acid pretreated corn stover by using *Thermoanaerobacterium thermosaccharolyticum* W16 as microbial inoculum, additionally, studied the effect of acid concentration and reaction time on hydrogen yield based on a 2^2 experimental design approach. The major findings of this thermophilic fermentation showed optimal conditions as 1.69 Wt% acid concentration and 117 min pretreatment time, and the peak hydrogen concentration of 2.24 mol H_2/mol sugar was attained. Similarly, On the other hand, biohydrogen production using corn stover by *T. thermosaccharolyticum* W16 integrated with NaOH pretreatment and cellulase enzymolysis resulted in 108.5 mmol/L H_2 as reported by [68], and also outcomes of the

hydrolysate-based fermentation concentration and HPR of 11.2 mmol/L h– were comparable with the results of experiments carried out with model sugar substrate solutions.

Liu and Cheng [69] employed mixed microbiome in the thermophilic H_2 fermentation of corn stover and suggested the sulfuric acid pretreatment with microwave irradiation. This combined method made a significant improvement and reach 1.53 mol H_2/mol glucose maximal yield by using 0.3 N H_2SO_4 and 45 min contact time, and this result is relatively higher than the H_2 yields of fermentations from untreated or acid pretreated corn stover.

Datar, Huang, Maness, Mohagheghi, Czernik and Chornet [70] presented mesophilic fermentation of liquid fraction of neutral and sulfuric acid pretreated corn stover assisted with steam-explosion. The turnovers showed that peak H_2 yield (3.0 mol H_2/mol glucose) could be reached from liquids of pretreated and acid-impregnated corn stover due to the release of more amount of monomeric sugar in contrast with the neutral treated substrate (2.84 mol H_2/mol glucose).

Pan, Zhang, Fan and Hou [71] investigated H_2 production from acid treated corncob as feedstock. The optimal pretreatment conditions were 1 wt% HCl and 100 °C for 30 min, which resulted in a maximal hydrogen yield of 107.9 mL/g TVS (TVS = 0.901 $W_{corncob}$) while the substrate concentration was 10 g/L. Wang, Wang, Feng, Wang and Huang [72] and Ma, Wang, Wang, Bu and Bai [73] studied the biohydrogen fermentation in a batch system with reactor size of 150 mL of acid (HCl) and enzymatically pretreated cornstalk substrate with special emphasis on the examination of main parameters (substrate concentration, initial pH, HCl concentration, enzymatic temperature and time) that could effect on H_2 production performances. In both the cases, the optimal pretreatment parameters has been found as 2 h long 0.6 wt % HCl treatment at

90 °C followed by a 72 h long enzymolysis at 50 °C and at 4.8 initial pH. Ma, Wang, Wang, Bu and Bai [73] reported that 164.48 mL/g TS maximal hydrogen yield with optimal substrate concentration of 10 g/L and 57.85% as H_2 percentage, via orthogonal design method, whereas [72] obtained an optimal concentration value at 20 g/L resulting 146.94 mL/g TS yield and 68.36 % as H_2 percentage from the same composition substrate during 15 h long fermentation (TS = 0.859 $W_{dried\ cornstalk}$). As it could be concluded, the substrate concentration plays a very important role during the fermentation reaction and affects the production yield.

Pan, Ma, Fan and Hou [74] produced hydrogen from a combination of dilute H_2SO_4 + enzyme for cornstalk biomass. The outcomes of the experimental design resulted that 209.8 mL/g TVS (TVS = 0.817 $W_{dried\ cornstalk}$, TS = 0.902 $W_{dried\ cornstalks}$) yield could be reached by using this pretreatment method with optimal parameters of 1.5 wt % H_2SO_4, 121 °C and 60 min at acidic conditions and 52 °C, 48 h and 4.8 initial pH during enzymatic phase.

Zhang, Fan, Xing, Pan, Zhang and Lay [75] used HCl boiling pretreatment without enzymatic hydrolysis (0.2 wt % acid, 30 min) for biohydrogen fermentation using corn stalk as a carbon source. They have found the optimal substrate concentration as 15 g/L, while the H_2 yield was 149.69 mL/g TVS (TVS = 0.8745 $W_{dried\ cornstalks}$), however, the H_2 percentage in the gas mixture was ranged between 45-56 %. Biological treatment of the substrate could be used as an alternative pretreatment method as represented in the earlier sections, but it consumes more time.

4.3 Ethanol

Conversion of lignocellulosic biomass to ethanol has been widely studied in past decades. New technologies are being proposed for lignocellulosic ethanol production, which includes mild torrefaction [76, 77]. Different processing methods have also been proposed after the pretreatment

step is done, which includes separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation, and consolidate bioprocessing (CBP) [76]. In CBP, lignocellulosic materials are depolymerized into sugars and simultaneously enzymes are produced and convert them to ethanol or other products in a single step. Brethauer et al. achieved 67% ethanol yield by dilute acid pretreatment of wheat straw using natural strains of microbes [78]. For ethanol production, organosolv pretreatment using ethanol is also preferred, as the used ethanol is recovered during distillation, where a final pure product is obtained, rather than lost during pretreatment steps [79, 80].

4.4 ABE fermentation

ABE fermentation converts sugars into products such as acetone, butanol, and ethanol (ABE) and usually be carried out after an appropriate pretreatment step [81-83]. ABE fermentation of NaOH-pretreated corncobs resulted in 350g ABE/kg [84]. Kumar et al. have performed a comparative economic analysis of ABE fermentation of different feedstocks including cellulosic and non-cellulosic based materials. Sugarcane-based substrates had a production cost of US$ 0.59/kg butanol, while for cellulosic materials it was US$ 0.75/kg butanol produced. Both substrates showed economic feasibility, which encourages industries to continue to use and develop this technology [85, 86].

5 Conclusions

Pretreatment of lignocellulosic biomass is essential for efficient release of bioenergy production. However, there are lot of uncertainties around it including formation of inhibitors, economic feasibility and environmental impacts to commercialize the process. A holistic view including techno-economic feasibility and environmental viability is necessary for the researchers and

scientists than looking at some minor issues. Pretreatment of lignocelluloses for bioenergy production has the potential for industrialization, with some pilot facilities under construction. However, the important aspects concerning commercialization are its economic, operative and logistic challenges, which need to be addressed soon. It is necessary to look at reducing energy consumption during pretreatment, and efficient release of sugars. Most pretreatment methods helps with increase in surface area of feedstocks after pretreatment however some pretreatments such as sulfuric acid and steam explosion have high effect in generating toxic compounds during pretreatment. Transforming the lignin from current use of fuel in boiler to technical lignin will enhance the economic feasibility.

Abbreviations:

ABE – Acetone Butanol Ethanol

AFEX – Ammonia Fiber Expansion

CBP – Consolidated Bioprocessing

HMF – Hydroxy Methyl Furfural

IL- Ionic Liquids

SHF – Separate Hydrolysis and Fermentation

SSF – Simultaneous Saccharification and Fermentation

TS- Total Solids

TVS – Total Volatile Solids

6 References

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List of figures

Figure 1. Different layers of cell walls present in plant cells adapted from [14].

Figure 2. Effect of pretreatment on (a) biomass cell wall structure adapted from [87]; and (b) enzyme hydrolysis (source Adapted from [28]).

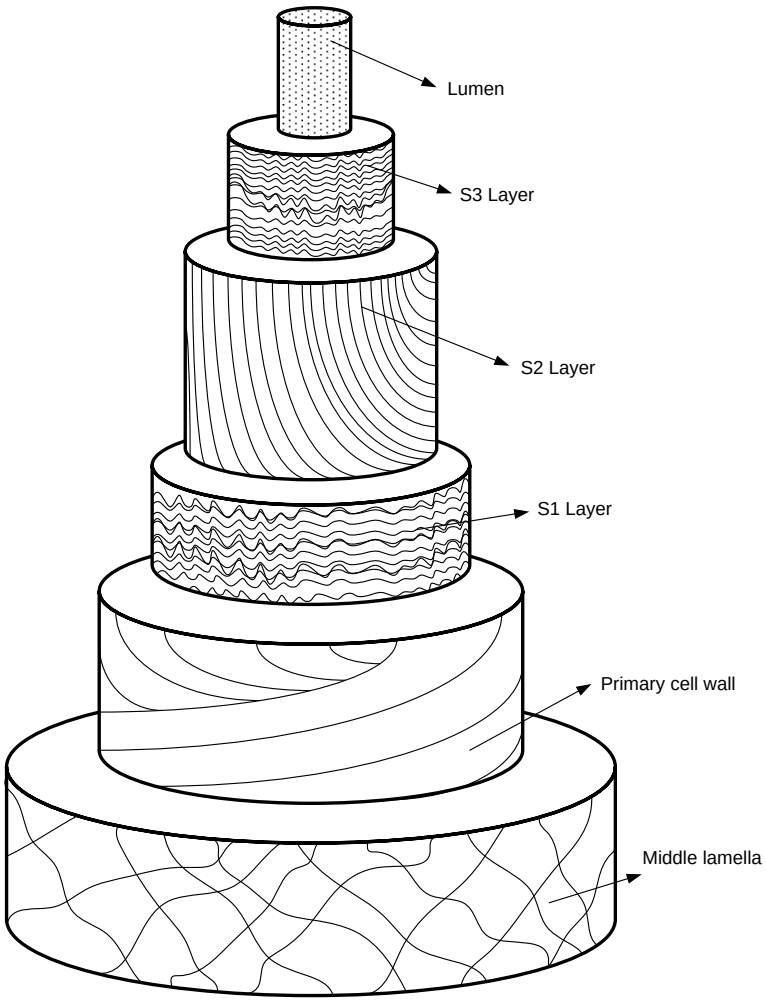
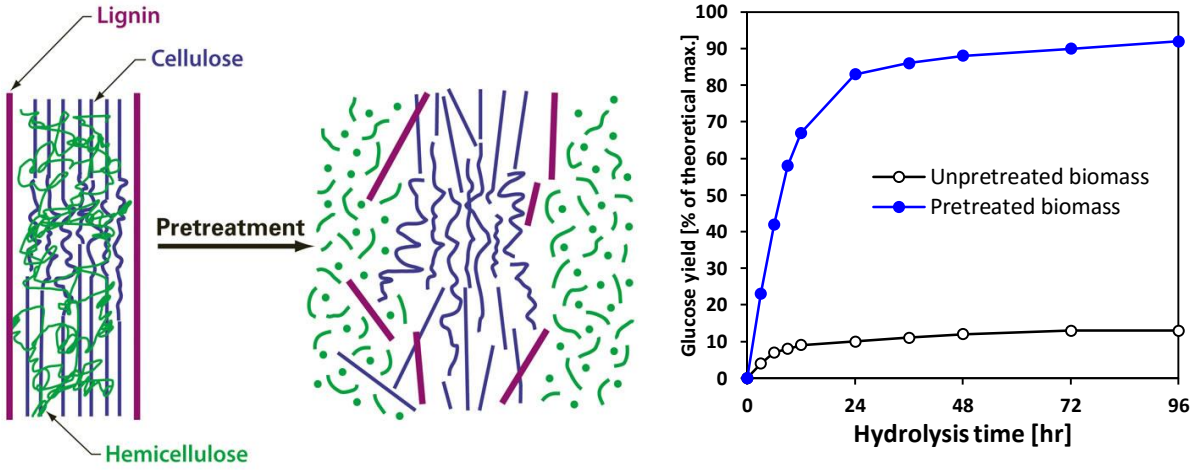

Lumen
S3 Layer
S2 Layer
S1 Layer
Primary cell wall
Middle lamella

Figure 1.


Lignin
Cellulose
Pretreatment
Hemicellulose
Glucose yield [% of theoretical max.]
Hydrolysis time [hr]
Unpretreated biomass
Pretreated biomass
0
10
20
30
40
50
60
70
80
90
100
0
24
48
72
96

(a) (b)

Figure 2.

Table 1. Composition of different lignocellulosic biomass adapted from [12]

Biomass	Cellulose (%)	Hemicellulose (%)	lignin (%)
Switchgrass	5–20	30–50	10–40
Miscanthus	38–40	18–24	24–25
General grasses	25–40	25–50	10–30
Municipal solid waste	33–49	9–16	10–14
Newspapers	40–55	25–40	18–30
Corn cob	42–45	35–39	14–15
Corn stover	38–40	24–26	7–19
Sugarcane bagasse	42–48	19–25	20–42
Rice straw	28–36	23–28	12–14
Wheat straw	33–38	26–32	17–19
Barley straw	31–45	27–38	14–19
Sweet sorghum bagasse	34–45	18–27	14–21
Oat straw	31–37	27–38	16–19
Rye straw	33–35	27–30	16–19
Rice husk	25–35	18–21	26–31
Softwood	27–30	35–40	25–30
Hardwood	20–25	45–50	20–25

Table 2 Different pretreatment method and their impacts on biomass

Pretreatment	Examples	Major impacts	Sources
Physical	Extrusion Freeze Irradiation Mechanical commination Microwave Sonication	Decreases the degree of polymerization. Reduces the crystalline structure of cellulose. Increases the surface area. Reduces the particle size	[88], [42], [43]
Thermochemical	Alkali Dilute acid Ionic liquids Organosolv Oxidative Ozone	Alters the lignin structure.Decreases the degree of polymerization. Reduces the crystalline structure of cellulose. Hydrolyzes the hemicellulose. Hydrolyses partially the cellulose.Solubilizes the hemicellulose.	[27],[88], [42]
Biological	Ensilage Enzymatic Fungal Microbial consortium	Alters the lignin structure. Reduces the degree of polymerization of hemicellulose and cellulose. Solubilizes the cellulose	[88], [42]
Other hybrid	Catalyzed steam ammonia fiber expansion AFEX Explosion Wet oxidation Steam explosion Liquid hot water	Alters the lignin structure. Decreases the degree of polymerization. Reduces the crystallinity of cellulose. Increases the surface area. Reduces the particle size. Reduces the degree of polymerization of hemicellulose and cellulose.	[27],[88], [43], [89]

Table 3. Different utility consumption and their costs for different lignocellulosic pretreatments adapted from [41].

Utility	Dilute Acid		Dilute Alkali		Hot Water		Steam Explosion	
	Amount (kg/L EtOH)	Cost (¢/L EtOH)	Amount (kg/L EtOH)	Cost (¢/L EtOH)	Amount (kg/L EtOH)	Cost (¢/L EtOH)	Amount (kg/L EtOH)	Cost (¢/L EtOH)
Electricity (KWh)	0.56	3.91	0.52	3.64	0.52	3.64	0.58	4.05
Steam	5.91	0.00	5.82	0.00	6.01	0.00	4.03	0.00
Cooling Water	500.24	2.50	500.50	2.50	570.00	2.85	401.44	2.00
Chilled Water	0.73	0.03	0.84	0.03	0.84	0.03	0.89	0.04
CT Water	88.76	0.62	89.04	0.62	89.23	0.63	98.94	0.69
Steam (High P)	0.42	0.00	0.42	0.00	0.42	0.00	0.62	0.00

Table 4. The different organic solvent used for lignocelluloses pretreatment and their effects.

Raw material	Organic acid	Catalyst	Time	Solids loading	Temperature	Cellulose yield	Kappa number	Reference
Bagasse	80% Acetic acid	Absence	60 min	10%	145°C	63%	44	[90]
Beech	90% Acetic acid	0.2% HCl	60 min	12%	130°C	50%		[91]
Marabou	90% Acetic acid	0.2% HCl	60 min	10%	-			[92]
Wheat straw	80% Acetic acid	0.92–13.5% Nitric acid	20 min	5%	120°C			[93]
Wheat straw	90% Acetic acid	4% H2SO4	180 min	10%	105°C	50%		[94]
Sugarcane straw	73–93% Acetic acid	0.3% HCl	300 min	16–30%	115°C			[95]
Populus	80% Formic acid	2% H2O2	105 min	12%	75°C	53.70%		[96]
Rice straw	80% Formic acid	Absence	60 min	8%	100°C	44.40%		[97]
Sugarcane bagasse	80% Formic acid	Absence	90 min	10%	85°C	45.50%	26.1	[98]
Cardoon stalk	80% Formic acid	5% H2O2	90 min	10%	60°C	62.60%	19	[99]
Sugarcane bagasse	10–100% Formic acid	mineral acids, acetic acid, and alkalis	90 min	5–30%	80–121°C	0.763 g/g reducing sugar		[100]
Corn	88% Formic acid	Absence	360 min	10%	60°C	85% hemicelluloses		[101]
Miscanthus	90% Formic acid	0.1% HCl	36 min	8%	-			[102]
Rice straw	2–25% Acetic acid	Absence	5 min	5–10%	-	71.4% sugar		[103]
Corn stover	50 and 90 mM acetic acid	Absence	30 min	10%	130–190°C	92-97% glucan		[104]
Triticale straw	50% Acetic acid and 30% Formic acid	Absence	180 min	8%	107°C	48.50%	33.8	[92]

Table 5. Effect of different pretreatments on lignocellulosic feedstock's (Adapted from [28]).

	Milling	Steam explosion	LHW	Acid	Alkaline	Oxidative	AFEX	ARP	Lime	CO_2 explosion
Increase in accessible surface area	H	H	H	H	H	H	H	H	H	H
Cellulose decrystallization	H	n.d.	n.d.	n.d.	n.d.	n.d.	H	H	n.d.	n.d.
Hemicellulose solubilization	n.d.	H	H	H	L	n.d.	M	M	M	H
Lignin removal	n.d.	M	L	M	M	M	H	H	H	n.d.
Generation of toxic compounds	n.d.	H	L	H	L	L	L	M	M	n.d.
Lignin structure alteration	n.d.	H	M	H	H	H	H	H	H	n.d.

H- high effect, M- moderate effect, L- low effect, n.d. - not determined