The Role of Physicochemical Pretreatment in Lignocellulosic Biomass Energy Valorisation – A Review

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ABSTRACT

The surging climate change caused by carbon dioxide emissions primarily from the use of fossil fuels poses a threat to the global economy and civilization. Furthermore, fossil fuels are rapidly depleting, prompting the need to explore alternative and sustainable energy sources. Lignocellulosic biomass is a renewable energy source whose potential remains underexploited. Harnessing biomass energy faces challenges that limit its economic exploitation. Limited knowledge to maximize its full potential and inefficiencies experienced through the experimental stages that affect full rollout and optimal performance. An efficient valorization of lignin and cellulose components of the biomass to desired energy products remains contingent on the effective depolymerization of the biomass through pretreatment intervention. Several studies have focused on pretreatment methods such as chemical, physical, and biological separately, while few have attempted to evaluate the effect of combined methods such as physicochemical that combines physical and chemical action in biomass pretreatment. This study characterizes the lignocellulosic biomass and reviews the commonly available physicochemical pretreatment methods for improving performance in bioenergy production. The reviews examine the performance of various techniques including steam explosion, liquid hot water, ammonia fiber explosion, CO_2 explosion, soaking in aqueous ammonia, and wet oxidation methods. Furthermore, the reviews focused on highlighting the performance criteria and comparing the benefits obtained from each technique.

Keywords: *Pretreatment, Lignocellulosic biomass, Physicochemical pretreatment, Bioenergy*

INTRODUCTION

Global efforts to minimize greenhouse gas discharges oblige the enhancement of more maintainable, green, and environmentally friendly energy substitutes. Following the depletion of fossil fuels and the attendant environmental issues, biomass research has become an appealing subject (Kurniawan *et al.*, 2014). Biomass is an organic material that is renewable and is derived from live or recently living organisms such as plants or animals (Benti *et al.*, 2021). During their growth, plant biomass produces a primary wall that is significant in offering structural functions such as protection, signal transduction, and interactions with neighboring cells (Alberts *et al.*, 2002; Zeng *et al.*, 2017). The primary wall contains a low proportion of cellulose but a greater presence of pectin that surrounds the growing and dividing plant cells (Alberts *et al.*, 2002; Sarkar *et al.*, 2009). Likewise, plant biomass also produces a secondary wall which provides strength and rigidity in plant tissues that have ceased growing (Sorieul *et al.*, 2016; Avci, 2022). In the wake of the exploration of renewable energy sources, biomass can be used as part of the energy supply chain (Helal *et al.*, 2023). Lignocellulosic biomass (LCB) as a feedstock is abundant (Dahmen *et al.*, 2019), inexpensive, and evenly distributed in nature.

The exploitation of LCB as an alternative bioenergy source from crop residues, such as; corn straw (Aghaei *et al.*, 2022), wheat straw (Taghizadeh-Alisaraei *et al.*, 2023), rice straw (Al-Haj Ibrahim, 2018), water hyacinth (Gaurav *et al.*, 2020) and other lignocellulosic biomasses from agricultural practices are on the rise due to its availability and accessibility (Amin *et al.*, 2017). LCB is a high-potential alternative energy source to avert dangers posed by fossil fuels through second-generation biofuels from feedstock that do not compromise global food security (Zoghlami & Paes, 2019). LCB possesses desirable plant biomass characteristics for bioenergy generation including high cellulose and low lignin, biodegradability, resistance to pests and diseases coupled with its assured perennial availability (Carlini *et al.*, 2018). However, its valorization can be limited by the recalcitrant nature associated with; rigid cell wall structure, crystalline cellular machinery, and lignin component, making it resistant to chemical and biological actions (Silveira *et al.*, 2013).

LCB pretreatment technologies focus on modifying the biomass structure to remove hemicellulose and lignin, making the carbohydrate fraction accessible to enzymatic hydrolysis for optimal bioenergy yield (Sharma *et al.*, 2023). Pretreatments may take the form of; physical, chemical, biological, or physicochemical techniques incorporating both physical and chemical interventions (Bensah & Mensah, 2019). Although each of the methods can be applied based on the prevailing conditions, the methods are not without unique challenges to

overcome (Antunes *et al*., 2019). Biological pretreatment methods, for example, are green and eco-friendly, but are inherently slow and difficult to scale up (Sharma *et al*., 2023), whereas physical pretreatment is associated with the inability to eliminate lignin content in LCB materials, rendering the cellulose content inaccessible (Brodeur *et al*., 2011; Saritha *et al*., 2012). Similarly, chemical pretreatments are distinguished by the loss of fermentable sugar due to an increase in the breakdown of complex substrates, the production of inhibitory byproducts as hydroxymethylfurfural (HMF) under very acidic conditions, and high chemical expenses, among other problems (Kucharska *et al*., 2018). As a result, an optimal pretreatment process must strike a compromise between three important parameters: efficiency, cost, and the formation of unwanted byproducts (Hernández-Beltrán *et al*., 2019).

This study characterizes the lignocellulosic biomass and reviews the existing common physicochemical pretreatment methods for enhanced performance in bioenergy production. The reviews examine the performance of different techniques including; steam explosion, liquid hot water, ammonia fiber explosion, CO2 explosion, soaking in aqueous ammonia, and wet oxidation methods. Further, the reviews focused on highlighting the performance criteria and comparing the derived benefits of each technique.

Lignocellulose biomass and its characteristics
Lignocellulosic materials can be obtained from plant feedstock, such as purposely grown energy crops (Sluiter *et al*., 2010) with examples of; corn stover, rice straw, and sugar cane bagasse (Kadam & McMillan, 2003; Adewuyi, 2022). Other examples of lignocellulosic energy plant biomasses include; miscanthus and switch grass which are present in huge amounts to provide biofuels, biochemicals, as well as animal feed (Saini *et al*., 2015). Despite the great effort invested in the improvement of lignocellulose material digestibility for positive green energy generation, the impact on efficiency, energy cost reduction, and adoption is yet to be realized (Adewuyi, 2022). The considered high cost of energy production from such biomass has been aggravated by its complexity despite its potential (Reid *et al*., 2020). The availability of various lignocellulosic materials with varying characteristics also calls for research to narrow down on best feedstock and capitalize on its production (Saini *et al*., 2015; Adewuyi, 2022). However, irrespective of the variability, the general characteristics conform to; 50-60% carbohydrates (cellulose and hemicellulose), and 20-30% lignin while the other minor components such as extractives, fatty acids, and ash comprise 10-30% (Galbe & Wellberg, 2019). **Figure 1**, illustrates the lignocellulose structure, an example of a bioenergy crop and its constituents.
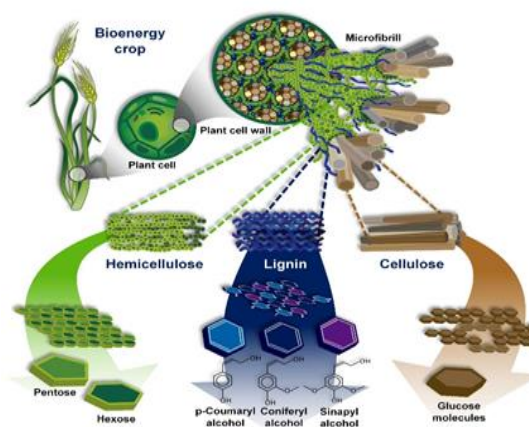
Figure 1. Structure of lignocellulosic biomass and its biopolymers.

Lignocellulose, which is developed with cellulose, hemicellulose, and lignin, is the fundamental building block of plant cell walls. Furthermore, the plant cell wall includes less pectin, protein, ash, and extractives. The cell wall also contains soluble non-structural materials like N, non-structural sugars, chlorophyll, and waxes. The general structure comprises polymers with different chemistry, and that perform different functions in the lignocellulosic plants. The total quantity for every constituent mentioned differs in various plant species and the part of the plant considered. For instance, hardwood and softwood stems have greater amounts of cellulose than grasses and nut shells, whereas their leaves contain more than 80% hemicellulose **(Table 1)**.

Table 1. Cellulose, hemicellulose, and lignin contents in common agricultural residues and waste (Kumar *et al*., 2009)

Lignocellulosic Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40-45	24-40	18-25
Softwood stems	45-50	25-35	25-35
Nutshells	25-30	25–30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper	85-99	0	0-15
Wheat straw	30	50	15
Sorted Refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspaper	40-45	25-40	18-30
Waste papers from chemical pulps	60-70	10-20	5-10
Primary wastewater solids	8-15		
Solid cattle manure	1.6-4.7	1.4–3.3	2.7–5.7
Coastal Bermuda grass	25	35.7	6.4

Switchgrass	45	31.4	12
Swine waste	6	28	na

Cellulose

Cellulose is the most abundant component of plant cells, with an unbranched polymer chain made up of glucose units linked by - 1, 4-glycosidic linkages that give the cell wall structure rigidity and stability (Rongpipi *et al.*, 2019). Polymerization can reach up to 14,000 glucose units, with each glucose unit rotated 180° relative to the next unit (Gautam *et al.*, 2010). The orientation and direction of the glucose units play an important role in determining their functionality (Van Schaftingen & Gerin, 2002). The connectivity between the glucose units is aided by two intra-chain hydrogen bonds and two to three inter-chain bonds which tightly pack and stabilize the structure cellulose structure (Khazraji & Robert, 2013). As a result, the cellulose chains form compact aggregates of three-dimensional microfibrils that are further stabilized by hydrogen and van der Waals links (Heise *et al.*, 2021). Every microfibril is made up of 30-36 parallel cellulose chains. **Figure 2** illustrates the chemical structure of cellulose.
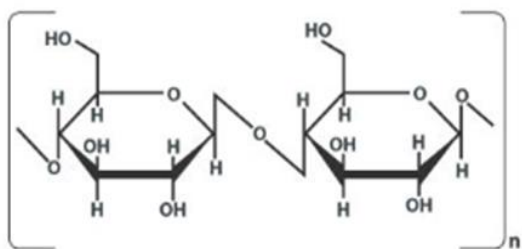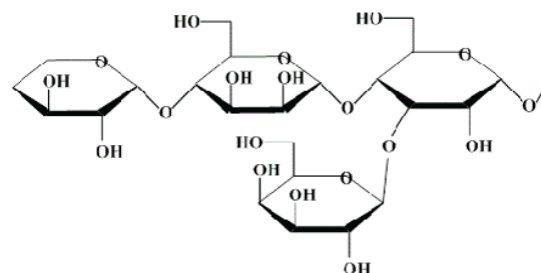

Figure 2. Cellulose Structure

Hemicellulose

Hemicellulose is a natural polymer found in lignocellulose biomass like cellulose, consisting of a variety of carbohydrate monomers (Lu *et al.*, 2021). Hemicellulose is present as the plant cell wall matrix that surrounds the cellulose skeleton (Zoghlami & Paes, 2019). Pentoses (such as xylose and arabinose) and hexoses (such as glucose, mannose, and galactose) make up the carbohydrate monomers (Navarro *et al.*, 2019). The contribution and composition of hemicelluloses change between plants and cells. Most hardwoods and agricultural plants, such as grasses and straw, have xylan as the dominating hemicellulose, whereas glucomannan and mannose are the predominant monomers in softwoods (Lu *et al.*, 2021). Xylan is the main component of heterogeneous polysaccharides in hemicellulose, which contains C5 and C6 sugars (Huang *et al.*, 2021). In hemicelluloses, the degree of polymerization of glucose units is between 100 and 200 units, which is substantially lower than in cellulose (Zoghlami & Paes, 2019). Unlike cellulose, the hemicellulose structure is more complex and characterized by many branches, predominantly of acetyl groups responsible for its noncrystalline nature, whereas cellulose is a linear polymer (Wohlert *et al.*, 2022). Hemicelluloses are highly hydrophilic, soluble in alkali, and easily hydrolyzed in acids (Huang *et al.*, 2021; Lu *et al.*, 2021). The hydrophilic nature of hemicelluloses relates to its acid groups that increase its water uptake in the fibers hampering the microbiological fiber degradation (Xu *et al.*, 2023). **Figure 3**, illustrates the chemical structure of hemicellulose $(C_5H_8O_4)_n$.

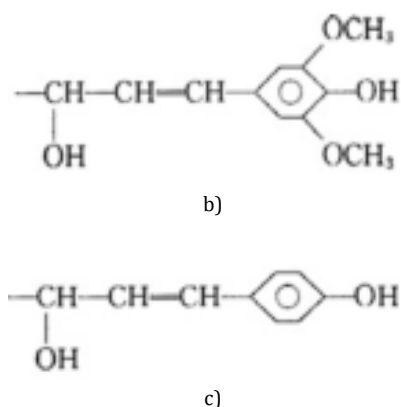

Figure 3. Hemicellulose Structure

Lignin

After cellulose and hemicellulose, lignin is the third most abundant building element of lignocellulose materials (Yang *et al.*, 2020). Lignin is an encrusting substance that acts as a protective layer on the plant cell wall and is known to inhibit anaerobic breakdown (Alberts *et al.*, 2002). The oxidation of phydroxycinnamyl alcohols: p-coumaryl, coniferyl, and sinap is required for the production of lignin. The lignin formation process can occur in three-fold biosynthesis dimensions involving; the shikimate pathway, phenylpropanoid pathway, and the synthesis of monolignols (Barros *et al.*, 2022). As a polymer binding the plant cell wall, lignin is considered a complex, amorphous, branched polymer constructed of different phenylpropane units (Aro *et al.*, 2005; Ganewatta *et al.*, 2019). Lignin's structure can exist as a three-dimensional mixture of p-coumaryl, coniferyl, and synapyl, based on their aromatic ring substitution pattern (Ralph *et al.*, 2019). The adaptability of lignin in the plant cell wall, caused by its three-dimensional composition and amorphous heteropolymers, protects the cell against structural stress, metabolic damage, and pathogenic attack (Gierlinger, 2014; Zeng *et al.*, 2017). Lignin can extremely be resistant to biodegradation as a result of the strong linkage bonds (Alberts *et al.*, 2002). Its component in lignocellulose biomass presents a challenge to efficient anaerobic digestion of the feedstock for biogas generation (Zheng *et al.*, 2014). Thus, lignin is an agent of low biomethanation of lignocellulose biomass and is known as a nuisance material for ethanol makers as it retards the enzymatic hydrolysis procedure. In addition, the native crystalline structure of cellulose can considerably limit its potential in cost competition as a precursor to biofuel production (Sasmal & Mohanty, 2018). **Figure 4** presents the chemical structure of three monomers of lignin: (a) p-coumaryl alcohol; (b) coniferyl alcohol; and (c). synapyl alcohol.


a)
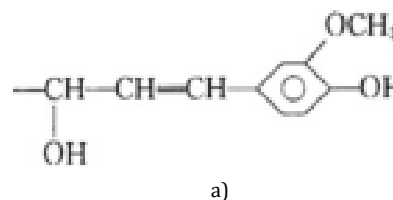
Figure 4. Lignin Chemical Structure. a) p-coumaryl alcohol.
b) coniferyl alcohol. c) synapyl alcohol

Pretreatment of lignocellulosic biomass
Pretreatment is an intervention process that rapidly disintegrates the lignocelluloses to its primary constituents such as; lignin, cellulose, and hemicellulose (Sasmal & Mohanty, 2018). The intricate structure of lignocellulose can limit microbial degradation and result in slow digestion and reduced

biogas yield (Omondi *et al*., 2019). Lignocellulosic and starch-based feedstocks require various forms of pretreatment to enhance biofuel and bioenergy production (Saritha *et al*., 2012). Pretreatment is an important tool for cellulose conversion processes and is essential to modify the structure of cellulosic biomass making cellulose more available to the enzymes responsible for the conversion of carbohydrate polymers into fermentable sugars (Mosier *et al*., 2005). The high cost and low efficiency of enzymatic hydrolysis of lignocellulosic feedstock are considered major impediments to ethanol production (Vasic *et al*., 2021). Pretreatment focuses on the disintegration and disruption of the crystalline and amorphous regions in the structure of cellulose and starch (Kumar *et al*., 2009), thus improving acid or enzyme access to carry out hydrolysis of the substrate (Maurya *et al*., 2015). Although it is difficult to single out the best pretreatment applicable in all situations, factors such as the high recovery of individual polymers and other compounds in the lignocellulosic material remain outstanding (Galbe & Wellberg, 2019). Additionally, reduction of secondary effect of toxic inhibitors must be minimized to avoid low enzymatic hydrolysis and fermentation (Kim *et al*., 2009; Brodeur *et al*., 2011). **Figure 5**, illustrates the action of pretreatment on lignocellulosic material and the resultant disintegration of the biomass structure.
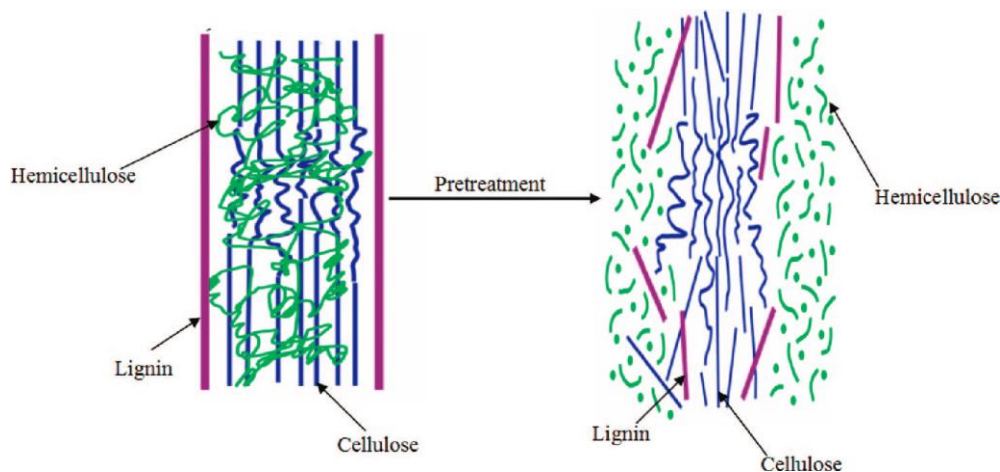
Figure 5. Schematic illustration of the role of pretreatment on lignocellulosic material (Kumar *et al*., 2009)

Based on treatment types and their applications, pretreatment processes are mainly categorized into three major categories, including physical, chemical, and biological treatments (Carlini *et al*., 2018). However, an additional method which is a hybrid of both physical and chemical treatments also exists as physicochemical methods (Brodeur *et al*., 2011). Generally, chemical pretreatment has received the most research interest based on its considered effectiveness and enhanced biodegradation of complex materials (Zhou *et al*., 2012). However, the chemical pretreatment is characterized by numerous setbacks including; destruction of lignin instead of separation, rising pH during digestion, buildup of salt, corrosiveness from acids, and overall development of process inhibitors (Pedersen & Meyer, 2010). The most popular chemical treatment methods include; alkaline pretreatment, acid pretreatment, ozonolysis pretreatment, and oxidation pretreatment (Deepanraj *et al*., 2014). Although many chemical

pretreatment methods have been studied for cellulosic ethanol production, only some of them have been applied to biogas production in AD processes (Zheng *et al*., 2014). Physicochemical treatments tend to create a balance between the chemical and physical methods to overcome challenges experienced by each method (Brodeur *et al*., 2011). The methods aim to affect both the physical parameters as well as their chemical bonding (bond cleavage) (Taylor *et al*., 2019). **Figure 6** summarizes the general approaches to LCB pretreatment for enhanced enzymatic hydrolysis and fermentation.
Primarily, the selection of an effective pretreatment method comprehensively depends on certain criteria and factors including; preservation of hemicellulose fractions, limiting the formation of inhibitors (Aftab *et al*., 2019), minimizing energy input, recovery of high-value-added co-products pretreatment catalyst and its recovery, among others (Baruah *et al*., 2018).

Overall, the chosen method must produce results that outweigh associated negative impacts leveraging on its ease of operation and associated costs (da Silva *et al.*, 2016).
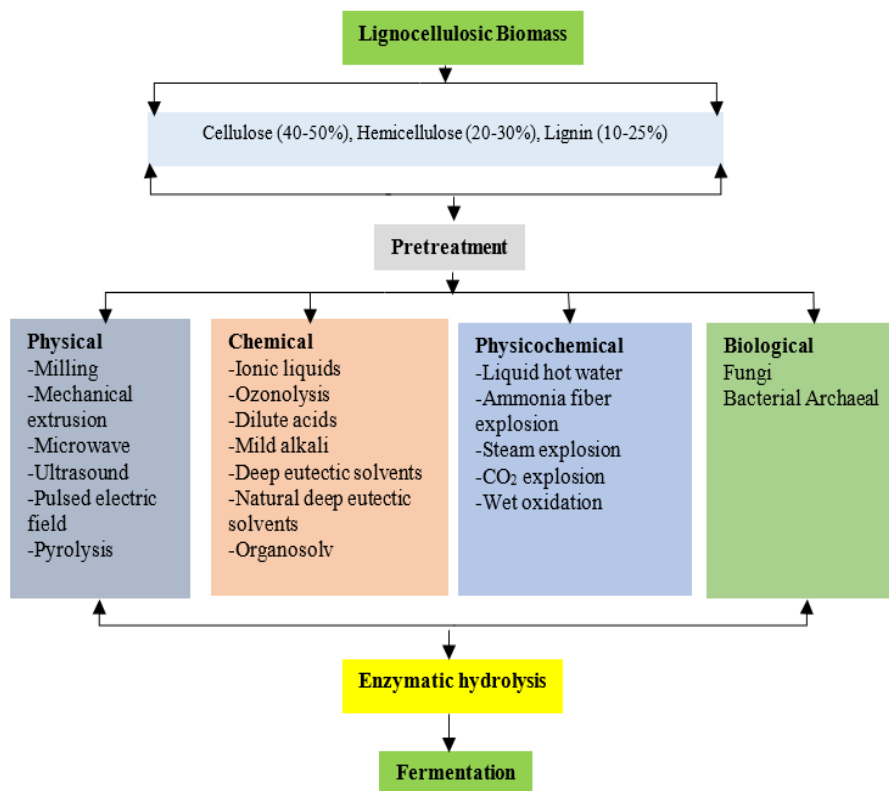

Figure 6. General approaches to lignocellulosic biomass Pretreatment

Physicochemical pretreatment

Physicochemical pretreatment is an applicable technique in enhancing the anaerobic digestion process through enhanced disintegration of complex organic wastes into simpler and more biodegradable constituents (Mitraka *et al.*, 2022). The pretreatment process promotes solubilization of the organic and inorganic compounds in the substrate (Kucharska *et al.*, 2018), thereby inducing hydrolysis while reducing the reactor volume (Taherzadeh & Karimi, 2008). The optimal thermal

pretreatment occurs at temperatures ranging from 160-200ºC in 30-60 min, with a caution to avoid temperatures above 250ºC associated with possible pyrolysis of the substrate (Branca & Blasi, 2023). Thermal pretreatments can be conducted through; steam explosion (SE), liquid hot water (LHW), ammonium fiber explosion (AFEX), soaking in aqueous ammonia (SAA), and irradiation methods. The Physicochemical pretreatment methods have advantages and disadvantages summarized in **Table 2**.

Table 2. Advantages and disadvantages of physicochemical pretreatment methods.

Method	Advantages	Disadvantages	References
Steam Explosion (SE),	- Low deteriorated byproduct yield with good hemicellulose production; avoidance of acid handling and recycling stages. -One of the most energy-efficient and environmentally friendly. -Lack of organic solvents and corrosive chemicals makes it attractive for industrial-scale use. -Lignin contains mainly phenolic monomers, making it easier to process afterward. -Applicability at an industrial scale.	-Hemicellulose fraction can partially be degraded at high pretreatment severities. -Formation of some inhibitory compounds for enzymatic hydrolysis. -Enzyme and yeast inhibitors generated during the pretreatment. -Incomplete deconstruction of the lignin-carbohydrate-complex. -High pressure and temperature requirement.	Teixeira *et al.* (2014); Chen and Liu (2015); Ziegler-Davin *et al.* (2021); Tan *et al.* (2021).

Ammonia Fiber Explosion (AFEX),	-Very effective in opening up cellulose to enzymatic attack. - The process increases porosity and surface area while selectively removing lignin without affecting the degradation of carbohydrates. -Decreases the synthesis of inhibitors. -Fewer enzymes are needed for the procedure.	-Recycling ammonia consumes a large amount of energy and contributes significantly to the process costs. -Reduced overall sugar yields due to severe degradation of hemicellulose sugars	Bals *et al.* (2010); Chundawat *et al.* (2020); Zhang *et al.* (2022)
CO₂ Explosion,	-Increases accessible surface area. - Availability at a reasonable price. -Reduced production of inhibitory substances. -Non-flammability. -Produces simple post-extraction recovery and environmental acceptability. -The solubilization of hemicellulose through adding the external acid provides partial cellulose hydrolysis. -Requires low temperature input.	-Very high-pressure requirements. -High requirement of equipment. -Inhibitory compounds may occur when using acids.	Brodeur *et al.* (2011); Kang *et al.* (2013); Maurya *et al.* (2015); Tan *et al.* (2021).
Liquid Hot Water (aquasolv),	- Increases the conversion of polysaccharides, particularly cellulose, into glucose with a minimal investment. The method yields pure hemicellulose. Does not require the addition of chemicals or catalysts. -Hydrolyzes hemicellulose, achieves a high yield of sugars. -Does not require washing, recovery, and detoxifying.	-Prone to the formation of inhibitive compounds as a limiting factor in the enzymatic activity and fermentation of microorganisms in the latter stages of the process. -Requires high energy.	Brodeur *et al.* (2011); Bensah and Mensah (2019); Chundawat *et al.* (2020); Tan *et al.* (2021).
Wet Oxidation,	-High degree of solubilization of hemicellulose and lignin. -Limited formation of degradation compounds. -Environmental-friendly with less side products.	-High cost of oxygen and alkaline catalyst. -Difficulty in separation of the solvents.	Maurya *et al.* (2015); Tan *et al.* (2021).

Steam explosion

Steam explosion (SE), also known as auto-hydrolysis, involves briefly heating biomass with high-pressure saturated steam. (Ziegler-Devin *et al.*, 2021). The heating temperature causes a catalytic reaction that breaks down the hemicellulose and changes the lignin content, preparing the substrate for hydrolysis (Zhang *et al.*, 2022). Organic acids like acetic acids and other acids made from acetyl or other functional groups enhance the hydrolysis of hemicellulose (Swiatek *et al.*, 2020; Huang *et al.*, 2021). Variables including moisture content, particle size, residence duration, and temperature can all affect how effective SE is. The typical pretreatment temperature ranges between 160-260 °C (Ziegler-Devin *et al.*, 2021), whereas the pressure range is between 0.6-4.83MPa (Ma *et al.*, 2022). As the pressure is progressively let go, the steam causes an expansion within the lignocellulosic matrix, upsetting the design of the cell membranes and causing the separation of individuals (Kumar *et al.*, 2009; Agbor *et al.*, 2011). The original biomass moisture content directly affects the length of pretreatment (Zhang *et al.*, 2022). However, according to Li *et al.* (2017), 2 to 10 minutes is usually the right amount of time. Waste biomass, such as paper waste, has frequently produced superior results with steam pretreatment (Elliston *et al.*, 2015; Zoubi *et al.,* 2023).

To enhance the efficacy of steam explosion, acid additives such as H_2SO_4, SO_2, and NaOH can be used to catalyze the process (Tan *et al.*, 2021; Yin *et al.*, 2021). In this process, catalysts can lead to a more complete solubilization/recovery of hemicellulose (Zheng *et al.*, 2014), a reduction in the generation of inhibitory chemicals (Jonsson *et al.*, 2013; Mai *et al.,* 2021), and an improvement in the biodegradability of lignocellulosic biomass (Rangel *et al.*, 2023). However, even without a chemical catalyst, water, which is used in steam generation also possesses acidic properties at high temperatures, and contributes the catalytic effect that aids the hemicellulose hydrolysis (Lu *et al.*, 2021). Acid addition is not mandatory and the SE process without acid addition is referred to as auto-hydrolysis (Amin *et al.*, 2017). One of the most popular pretreatment techniques for lignocellulosic biomass is steam explosion.

To determine the extent of SE in the pretreatment of biomass, a "severity factor" (log R₀), is used to measure the severity of the process. The harshness factor incorporates the effect of temp and the pretreatment duration in the pretreatment process. Equation 1 below presents the severity factor.

$$\log \mathrm{Ro} = \log(t * e(\frac{(T-100)}{14.75})) \qquad (1)$$

Place log The severity factor for SE is called Ro, and it ranges from 3.14 to 3.56 depending on how long the therapy is, T is the temperature (°C), t is the residence time (in minutes), and 14.75 is the activation energy under the current conditions, where the process complies with first-order kinetics and the Arrhenius law. 100 °C is the reference temperature at which no solubilization occurs (Amin *et al.*, 2017).

Steam explosion pretreatment has reported significant results on different biomasses. For instance, Barbanera *et al.* (2014) studied the impact of SE pretreatment on the generation of sugar from the enzymatic hydrolysis of olive tree pruning. The experiment includes pretreating the biomass at seven different levels of severity before enzymatic hydrolysis. The findings led to a predicted ethanol production of 14.41 g/100 g raw material at a severity level of 4.41. In another study, Pielhop *et al.* (2016), evaluated the effect of SE pretreatment on softwood to

comprehend the influence of explosive decompression on enzymatic digestibility. The findings presented that the intensity of the pretreatment and the pressure differential of the explosion are two important parameters that influence enzymatic digestibility. According to the study's findings, pretreatment with SE improves the enzymatic digestibility of refractory biomass, such as softwood.

Liquid hot water (Hydrothermolysis)

LHW pretreatment method involves subjecting the biomass to a high temperature of heated water at high pressure (Jimenez-Gutierrez et al., 2021). The process targets breaking the biomass cell structure, hydration of cellulose, solubilizing of hemicellulose, and incomplete elimination of lignin materials (Kim *et al.*, 2009; Kale *et al.,* 2021). Further, the process also focuses on the suppression of inhibitor formations. Effectively, the action leads to enhanced cellulose accessibility and susceptibility, leading to better microbial and enzyme degradation (Kim *et al.*, 2009). The technique is a hydrothermal method of pretreatment that does not require the addition of chemicals (Chen *et al.*, 2022). The method has widely been used in the pulp industry and for bioethanol production (Broda *et al.*, 2022). The optimal pH condition for LHW is preferably between 4-7 to minimize the monosaccharides formation and catalyze hydrolysis of the cellulosic material in the pretreatment process (Taherzadeh & Karimi, 2008; Maurya *et al.*, 2015). The usage of a high amount of water in this method enhances the solubilized products while lowering product concentration (Serna-Loaiza *et al.*, 2022). LHW has widely been applied in pretreatment studies for biomethanation of various feedstalks such as; Municipal solid waste (Perez-Pimienta *et al.*, 2017), microalgae, sugarcane bagasse (Gurgel *et al.*, 2014).

Jimenez-Gutierrez et al.'s study from 2021 examined the effects of LHW before management on poplar wood chips biomass on a small scale. At Temps going from 180 to 188 °C, pretreatment times between 30 and 240 min were investigated. The liquid and solid fractions gained after pretreatment were analyzed for acetic acid, which led to a full deacetylation of the poplar biomass. Similar to this, Li *et al.*'s (2017) research looked into the impact of LHW pretreatment on the chemical-structural change and decreased recalcitrance in poplar. The study found that LHW can significantly reduce the lignocellulosic biomass's cell wall resistance by improving the conversion of polysaccharides, notably cellulose, into glucose at a negligibly high initial investment. The research also demonstrated that xylan solubilization, hemicellulose molecular weight reduction, cellulose degree of polymerization, and the cleavage of alkyl-aryl ether bonds in lignin as a result of LHW pretreatment are significant factors linked to decreased cell wall recalcitrance.

Ammonia fiber explosion (AFEX)

The ammonia fiber explosion (AFEX), described by Brodeur *et al.* (2011), is a physicochemical pretreatment method in which biomass material is subjected to liquid anhydrous ammonia at high pressures and moderate temperatures before being quickly depressurized. 60 to 120 °C, the appropriate mild temperature is lower than that of a steam explosion (Chundawat *et al.*, 2020). The pretreatment approach aims to increase the pretreated material's digestibility through cellulolytic enzymes and/or microorganisms (Maurya *et al.*, 2015; Chundawat *et al.*, 2020). AFEX is a promising method for pretreating agricultural

material of lignocellulosic nature, for bioenergy production (Kucharska *et al.*, 2018). The main process parameters that control AFEX include; the reaction temperature, substrate residence time, ammonia loading, and water loading (Bals *et al.*, 2010; Dong *et al.*, 2022). The process focuses on the decrystallization of the cellulose, hydrolysis of hemicellulose, depolymerization of lignin (Questell-Santiago *et al.*, 2020), and increase of size and number of micropores in the biomass cell wall, boosting enzymatic hydrolysis rate noticeably as a result (Harun *et al.*, 2013). The AFEX pretreatment method does not always remove lignin and other substances from the biomass; instead, it causes the cleavage of lignin-carbohydrate complexes and the deposition of lignin on the surface of the material, which may prevent cellulases from converting the biomass into cellulose.

Teymouri *et al.* (2004) looked at how AFEX treatment affected the activity of *Acidothermus cellulolyticus* endoglucanase in transgenic plants. Tobacco leaves treated with AFEX and left untreated were tested for endoglucanase from *Acidothermus cellulolyticus* to see how the treatment affected the enzyme's activity. At 60 °C, with a 0.5:1 ammonia loading and 40% moisture content, the investigation was run. The study found that AFEX pretreatment was unsuitable for the release of cellulose enzymes from transgenic plants and estimated the maximum activity retention in AFEX at about 35%. In another study to determine the AFEX Pretreatment and Enzymatic Hydrolysis on canary grass, Bradshaw *et al.* (2007), Compared to their untreated controls, tests were performed on enzyme digestibility and potential improvements in sugar conversions. The most efficient AFEX treatment settings were identified through testing employing 168 h hydrolysis and 15 filter paper units of Spezyme CP cellulase/g glucan. The study determined that 100 °C, 60% moisture content, a dry matter to ammonia ratio of 1.2:1 kg, and canary grass growing age of seed stage were the ideal conditions for AFEX activation. Alizadeh *et al.* (2005) conducted a comparison study to examine the effects of AFEX on switch grass, and they determined the ideal conditions to be a reactor temp of 100 °C, an ammonia loading rate of 1:1 kg (ammonia: dry matter), and an 80% moisture level. The switch grass AFEX treatment increased ethanol production by 150%.

Soaking in aqueous ammonia (SAA)

Delignification of lignocellulosic biomass using the soaking aqueous ammonia (SAA) process improves hydrolysis and biomass-to-energy conversion without having a major impact on the amount of carbohydrates present (Kim *et al.*, 2009). The preference for ammonia-based pretreatment revolves around the advantage of retained cellulose and hemicellulose in the treated biomass (Latif *et al.*, 2018), making it suitable for simultaneous saccharification and co-fermentation (Isci *et al.*, 2008). Similarly, ammonia-based pretreatment has become a preferable method due to its high potential in the post-pretreatment effect and future commercial utilization (Zhu *et al.*, 2014; Latif *et al.*, 2018). The pretreatment method can alter the original biomass structure by inducing cellulose swelling and lignin and hemicellulose solubilization leading to cellulose exposure to enzymatic action (Akus-Szylberg & Zawadzki, 2021). Pretreatment by soaking in ammonia occurs in two forms: high severity, low contact time process (ammonia recycle percolation; ARP) and low severity, high treatment time process

(soaking in aqueous ammonia; SAA) (Kim *et al.*, 2009). During SAA pretreatment, high temperatures can result in a variety of different reactions, such as the dissolution of poorly graded polysaccharides, peeling of end groups and the formation of alkali stable end groups, alkaline hydrolysis of glycosidic bonds and acetyl groups, and the degradation and decomposition of both dissolved polysaccharides and peeled monosaccharides. (Wang *et al.*, 2013; Subhedar & Gogate, 2014).

Norwell *et al.* (2018), conducted a study to ascertain how entire maize kernels should be prepped for the synthesis of cellulosic ethanol from fiber fractions. Whole maize kernels were immersed in aqueous ammonia solutions containing 2.5, 5.0, 7.5, and 10% wt of ammonia at 100 °C for 24 hours as part of the investigation. According to the findings, pretreatment with ammonia at a 7.5% weight of ammonia increased ethanol production from 334 g/kg to 379 g/kg of maize or a 14% increase. In a similar study by Akus-Szylberg *et al.* (2021), SAA pretreatment of corn stover resulted in 38.7% and 68.9% delignification of biomass treated at 50 °C and 90 °C, respectively. The results showed a significant impact of SAA pretreatment on biomass delignification.

CO$_2$ explosion (Supercritical fluid pretreatment)

This is a technique developed to improve the pretreatment of lignocellulosic biomass using supercritical CO$_2$ explosion which reduces temperature demand lower than what is required for steam explosion and eventually lowers the cost (Srinivasan & Ju, 2010). The supercritical CO$_2$ takes the form of a fluid, however, compressed in a gaseous state at temperatures higher than its critical point (Pu *et al.*, 2022). The method is based on the knowledge that CO2 molecules, which are smaller than water and ammonia molecules, may be able to enter tiny holes in biomass (Maurya *et al.*, 2015; Morais *et al.*, 2015). Hemicellulose and cellulose are hydrolyzed using CO$_2$, and the low temperature used in the procedure prevents the acid from breaking down monosaccharides (Brodeur *et al.*, 2011; Mussatto *et al.*, 2021). The action mechanism for supercritical CO$_2$ entails the penetration of biomass micro pores under pressure and the rapture of the pores upon the pressure release (Aftab *et al.*, 2019). These findings in the contact of cellulose surfaces to cellulose enzymes during the hydrolysis stage. CO$_2$ is considered a green solvent with its critical temperature T_c being 31.0 °C compared with 374.2 and 243.1°C for water and ethanol respectively (Gu *et al.*, 2013). Unlike steam explosions characterized by high temperatures causing degradation of sugars, low-temperature conditions for CO$_2$ explosion prevent such sugar degradation (Brodeur *et al.*, 2011). Supercritical CO$_2$ has effectively been used as a green and non-flammable solvent for chemical reactions and separations (Gu *et al.*, 2013).

The effects of CO2-added ammonia explosion on the pretreatment of rice straw for bioethanol production were examined in a study by Cha *et al.* (2014). With a maximum glucose production of 93.6% for a 14.3% ammonia content, 2.2 MPa of CO$_2$ loading level, 165.1 °C of temperature, and 69.8 min of residence time, the study's pretreatment parameters were maximized. For the biomass, a scanning electron microscope revealed much more pores and surface area, enhancing enzyme accessibility for enzymatic saccharification. Finally, the study achieved a 97% ethanol yield through saccharification and fermentation. Similarly, a study by Zheng *et al.* (1998), investigated pretreatment for cellulose by CO$_2$ and realized a

disruption of cellulosic structure on biomass increasing accessible surface area to enzymatic hydrolysis. The results indicated the suitability of supercritical CO$_2$ in cellulose pretreatment. Additionally, a rise in pressure made it possible for CO$_2$ to enter the crystalline structure more quickly, yielding more glucose following pretreatment. In a separate study by Srinivasan and Ju (2010), supercritical CO$_2$ pretreatment for guayule grass was examined. This method outperformed others and produced much higher overall sugar yields for guayule (77% for glucose and 86% for all reducing sugars) via both pretreatment and hydrolysis. Compared to a dilute acid pretreatment, which only produced results of (50% for glucose and 52% for total sugars), the results were significantly superior.

Wet oxidation

Wet oxidation (WO) entails the treatment of lignocellulosic biomass with water and air at temperatures ranging between 170-200 °C and pressures of 0.5-2.0 MPa, for a residence time of 10-15 minutes (Refaat, 2012). According to Peral (2016), WO is used as an alternative to Steam Explosion as it aims to convert hemicellulose and lignin to oxidized compounds, e.g., CO$_2$, H$_2$O, alcohols and low molecular weight carboxylic acids. It facilitates the disintegration of cellulose after a significant amount of hemicellulose and lignin have been solubilized (de Jong & Gosselink, 2014), with the amount of lignin removed after pretreatment ranging from 50-70% depending on the type of biomass used and the prevailing conditions for the process.

In comparison to Steam Explosion and Liquid Hot Water pretreatment methods, WO produces lower amounts of furfural and 5-HMF (Refaat, 2012), which are strong inhibitors of the fermentation process (Peral, 2016). When combined with other methods such as Steam Explosion, larger particle sizes as well as higher biomass loadings can undergo energy valorization (Brodeur *et al.*, 2011). Further, the addition of oxygen at temperatures above 170 °C results in an exothermic process resulting in a reduction in total energy demand (Tomás-Pejó *et al.*, 2011). Chen and Wang (2017) suggested that this method of pretreatment enhances the sensitivity of the biomass to enzymatic hydrolysis thus resulting in higher enzymatic convertibility (de Jong & Gosselink, 2014). However, Tomás-Pejó *et al.* (2011) highlighted that WO does not catalyze hydrolysis of solubilized hemicellulose. Subsequently, it uses a significantly large amount of oxygen hence making it relatively expensive for commercialization (Merklein *et al.*, 2016).

The method has successfully been used in the pretreatment of wheat straw, newspaper waste, rice husk, sugarcane bagasse, and maize silage, among other organic matters (Zhang *et al.*, 2020). For wheat straw, for instance, the author highlighted that the released glucose from the smallest particles attained 90% of the theoretical maximum after a 24-hour enzymatic hydrolysis (Peral, 2016). It was also mentioned that WO was employed industrially for the treatment of wastewater and soil remediation by the oxidation of suspended particulates, which might then be used for energy production. McGinnis *et al.* (1983) used WO on a variety of low-grade hardwoods, including loblolly pine, black oak, and hemlock, and discovered that the procedure was successful in separating the cellulose, hemicellulose, and lignin components of the wood.

CONCLUSION

Physicochemical pretreatment methods can overcome the recalcitrance of LCB, by separating the cellulose from the matrix polymers, expanding the surface area that is available for enzymatic hydrolysis, decrystallizing cellulose, and separating hemicellulose and lignin. Physicochemical pretreatment methods promote a reduction of inherent moisture and particle size in the biomass, thereby enhancing its downstream valorization for energy production. The techniques involved, enhance the efficiency of biological activities for maximized energy generation through enzymatic processes. Whereas most reviews in the past, have focused on pretreatment techniques independently, a synergistic approach involving a combined compatible action by different methods such as through physicochemical methods, promises better results. The diversity in properties of lignocellulosic biomass demands a balanced action of more than one technique, thus the applicability of physicochemical methods which comprise both physical and chemical intervention. The choice of the specific method grossly depends on its efficiency and cost. Additionally, the choice of a pretreatment method should focus on integrated techniques capable of minimizing the inhibitor effects often a major drawback to pretreatment success. The most common setback in most pretreatment processes involves buildup of inhibitors that reduce saccharification by soluble lignin-derived phenolics, non-productive adsorption of enzymes on insoluble lignin, or low enzyme accessibility to cellulose occasioned by insoluble lignin hindrance. Deriving maximum benefits from the physicochemical pretreatment of lignocellulosic biomass demands intense exploitation of emerging and promising combined techniques that rely on the physiochemical fractionation of the biomass. The process description, benefits, disadvantages, and innovations used to address innate technological, economic, and environmental issues should take center stage in the thorough analysis. The physicochemical techniques examined in this study, such as soaking in aqueous ammonia (SAA), ammonium fiber explosion (AFEX), and liquid hot water (LHW), reveal highly promising results.

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