

## PRETREATMENT PROCEDURES ON LIGNOCELLULOSIC BIOMASS MATERIAL FOR BIOGAS PRODUCTION: A REVIEW

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**Abstract.** Lignocellulosic biomass materials are ample, sustainable and renewable assets with potentially far-reaching amounts of energy. They are an interesting option to fossil fuels which allows manufacture of biofuels and other organic compounds. Only specific and targeted pretreatment processes can ensure effective degradation of these lignocellulosic biomass material. Pretreatment procedures are necessary because they are the specific solution to the recalcitrance of biomass materials. It directly influences the biogas production potential. These procedures consist of physical, chemical, physico-chemical, biological or nanotechnological methods; emerging combined methods of lignocellulosic biomass pretreatment equally exist. Toxic inhibitors make up part of the drawbacks faced during pretreatment due to the fact that they immobilize cellulase and impede the growth of fermentative microbial consortia. There is therefore a dire need to either remove these inhibitors or reduce their presence. Enhanced production of biogas is very much dependent of the type of biomass involved, the pretreatment method used and the volume of toxic inhibitors generated. This review intends to help grasp the potential of pretreatment procedures and combinations of the same and their impact on the production efficiency of biogas and help to outline approaches to handling the emission of toxic inhibitors during the process solving the challenges that have to do with inefficient pretreatment results.

**Key words:** lignocellulosic biomass material; biogas; pretreatment; toxic inhibitors.

### INTRODUCTION

Lignocellulosic biomass material (LBM) are organic substances produced during photosynthesis in plants. Wood, sugar cane, bagasse, rice husks and straw, waste paper, corn cobs, animal and municipal waste, sewage and algae are some examples of these bio-materials. Lignocellulosic biomass material is part of the dry matter of plant [18]. They comprise cellulose (40-50%), hemicellulose (25-30%), lignin (15-20%) and small amounts of pectin, nitrogen-based compounds and inorganic components that are intertwined [62]. Plants rely on cellulose, a polymer, for structural support; hemicellulose serves as a binder and lignin sees to the overall stability of the structure [51, 68]. Due to their quantity, availability, accessibility and significant economic potential, lignocellulosic materials are being used more and more, however it is difficult to use lignocellulosic biomass material for energy production in its natural state due to its recalcitrance, therefore it is necessary to get past its obstinate property in order to convert it [57, 83].

Pretreatment is frequently necessary for easing this peculiarity. The economics of energy production processes from biomass depend greatly on pretreatment, which causes physical, chemical and structural changes in biomass [6, 7]. The amorphous region is increased during pretreatment, which makes hydrolysis easier. In order to facilitate chemical and enzymatic hydrolysis, it also increases the porosity of the internal matrix. Finally, it releases cellulose from lignin and hemicellulose [82]. Pretreatment is thus a tried-and-true method to enhance the degradation of such waste. According to Cheah *et al.* [13], common pretreatment techniques include physical (such as heat/pressure,

irradiation, ultrasonic), chemical (such as acids/bases, ozonation, oxidation), and biological (such as fungi, bacteria, enzymes addition under aerobic or anaerobic conditions) even nanotechnological methods now exist.

### BASICS OF LIGNOCELLULOSIC BIOMASS MATERIAL

Lignocellulosic biomass material (LBM) which contains roughly 50-75% methane and 25-50% carbon dioxide is a plentiful organic material good for the sustainable production of bio-energy and biogas. The world's most cost effective and renewable natural resource is lignocellulosic biomass. For the sake of human survival, it is crucial to develop renewable energy sources derived from lignocellulosic biomass as an alternative to fossil fuels [69].

The energy content of nearly 50% of the world's LBM biomass exceeds the basic energy needs of the entire planet [65], and it does not enter the human food chain. Energy crops (such as switch grass) and agricultural waste (such as corn stalks) are all potential sources of biomass. The chemical and biotechnology industries find LBM to be an appealing bulk material due to its characteristics there are a number of technical difficulties associated with LBMs industrial application [58]. The development of an effective method for separating lignin, hemicellulose and cellulose and turning the fractionated LBM into monomeric substrates that can be used right away for chemical production are the first challenges in using LBM [58].

The majority of the woody cell wall of plants known as LBM, are made up of polysaccharides, phenolic polymers and proteins.

This dense structure created by hemicellulose, lignin and cellulose are enclosed in the complex spatial composition of LBMs [93]. LBM is typically categorized into three groups: energy crops, biomass and virgin biomass. The pure biomass category comprises trees, shrubs and sand grasses, while the waste biomass category includes bagasse, sturgeon also waste from agriculture. Due to their high biomass productivity, energy crops are the feed stock used to create second-generation biofuels [93]. Production of biofuel and energy from LBM relies on the two main pathways. In LBMs with a Carbon to Nitrogen ratio of smaller than 30 and a liquid composition of more than 30%, biochemical processes are typically handled by microorganisms, fungi and enzymes. When available LBM has a Carbon to Nitrogen ratio more than 30 and a liquid composition lower than 30%, a thermo-chemical process is an alternative. Recent years have seen the development of new biofuels from LBM, including biohydrogen, butanol, dimethylfuran and gamma- valerolactone [93].

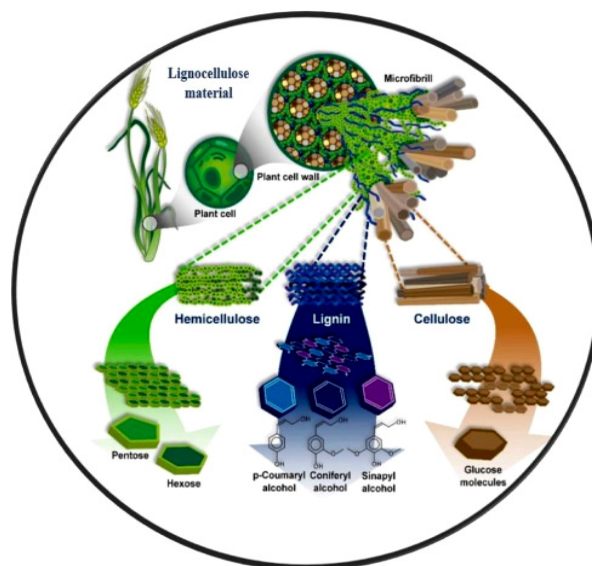


Figure 1. Showing structural layout of Lignocellulosic biomass material (culled from Khan *et al.* 2022 [pp. 4])

## COMPOSITION AND PATTERN OF LIGNOCELLULOSIC BIOMASS

The internal structure of lignocellulosic biomass can be seen to contain crystalline cellulose fiber that serves as the heart of the intricate structure of plant biomass. Hemicellulose lies in between the micro and macro fibrils of the cellulose matrix while cellulose and hemicellulose are both enclosed by lignin, which has a structural role (Fig. 1).

Depending on where the biomass comes from, the composition of the biomass varies greatly. Other small components such as extracts, proteins, water and inorganic components like silicon (Si), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) and aluminum (Al), exist alongside the three main components of LBM. These minor constituents all play a small function in forming the overall make-up of the biomass. The organic constituents of various LBM are summed up in Table 1.

## CHARACTERIZATION OF LIGNOCELLULOSIC BIOMASS MATERIAL

There is a huge variety in the physical and chemical characteristics of biomass feed stocks; they are discussed in terms of proximate, ultimate and compositional analysis all of which are crucial when describing any biomass to biofuel conversion process.

### PROXIMATE PROPERTIES

Most air-dried biomass has between 15% and 20% moisture. Total solids content (TSS) of biomass makes up the remaining portion of the fraction. Volatile solids (VS) and trace amounts of minerals (ash) make up total solids. Only a small portion of VS is converted during any kind of energy conversion process.

Table 1. Shows the content percentage of organic fractions of diverse lignocellulosic biomass material based on their dry weight

Biomass	Cellulose %	Hemicellulose %	Lignin %	References
Switchgrass	5 - 20	30- 50	10 - 40	[81]
Miscanthus	38 -40	18 - 24	24 - 25	[81]
Corn cob	42 -45	35 - 39	14 - 15	[81]
Corn stover	36 - 40	24 - 35	17 - 19	[72]
Sugarcane bagasse	42 -48	20 - 27	20 - 30	[22, 47]
Rice straw	28 - 36	21 - 28	20 - 28	[32]
Wheat straw	33 - 39	20 - 32	17 - 20	[87]
Barley straw	31 - 45	27 - 38	14 - 19	[72]
Sweet sorghum bagasse	34 - 45	18 - 27	14 - 21	[47, 85]
Oat straw	31 - 37	27 - 38	16 - 19	[81]
Rye straw	33 - 35	27 - 30	16 - 19	[81]
Rice husk	25 - 35	18 - 21	26 - 31	[81]

### ULTIMATE PROPERTIES

Most of the components of biomass are carbon, oxygen and hydrogen. According to the biomass's dry weight, it typically contains 35-50% carbon and 40-45% oxygen by mass. The quality and quantity of products produced during the conversion of biomass to biofuel depend on the biomass's final characteristics [93].

The resilience of biomass, which primarily made up of cellulose and hemicellulose, is correlated with the quantity of lignin and its constituents, syringol and guaiacol. These chemical compounds make the process of degradation problematic and challenging. Despite this, lignocellulose's hemicellulose is part of the material that is least resistant to heat and chemical processing (Fig. 2).

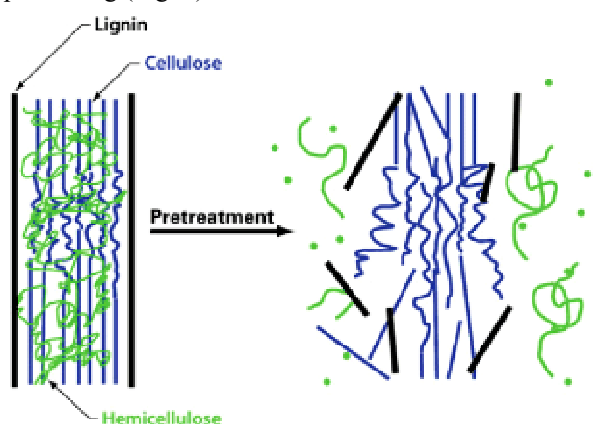


Figure 2. Shows the impact of pretreatment procedures on lignocellulosic biomass (cullled from Sudhavar and Naik, 2022 [pp. 114])

### PRETREATMENT APPROACHES ON LIGNOCELLULOSIC BIOMASS

The properties of biomass must be improved in order to increase its energy utilization efficiency [6].

The origin of the biomass and how it will be used in bio-conversion and biorefinery processes must be specifically considered when selecting pretreatment techniques. The two main challenges encountered with pretreatment technologies are how to recover pretreated products with little degradation of essential ingredients and high costs. Extensive research has been suggested in order to develop techniques that will allow us to more effectively utilize physical, chemical and biological pretreatment approaches because these issues have not yet been satisfactorily addressed by previous and current research and development. Reducing the lignocellulosic matrix's elasticity in an economical and environmentally friendly way is a crucial pretreatment step [56]. In recent years, research has increase on novel ways to process lignocellulosic biomass for fuel, energy and materials [82]. According to Jaramillo and Sanchez [34], pretreatment is needed to remove cellulose lignin matrix, reduce crystalline cellulose layer and boost the amount of amorphous cellulose (Fig. 3).

Since the attributes of LBM vary, the pretreatment approaches may vary too. A lot of learning and work is currently going on with respect to treatment and pretreatment techniques which could be best fitted for the absolute breakdown of LBM [54]. Pretreatment approaches fall majorly into categories physical, chemical and biological mechanisms. These mechanisms can equally be combined, producing a synergistic effect all in a bid to overcome the challenges that accompany pretreatment. The sole intention of trying out combined processes is to have higher conversion efficiency. Combined approaches could be physical methods with chemical methods, physiochemical methods and even nanotechnological methods. Whichever method is chosen will depend on the choice of the biomass, must be cost effective, environmentally friendly and safe.

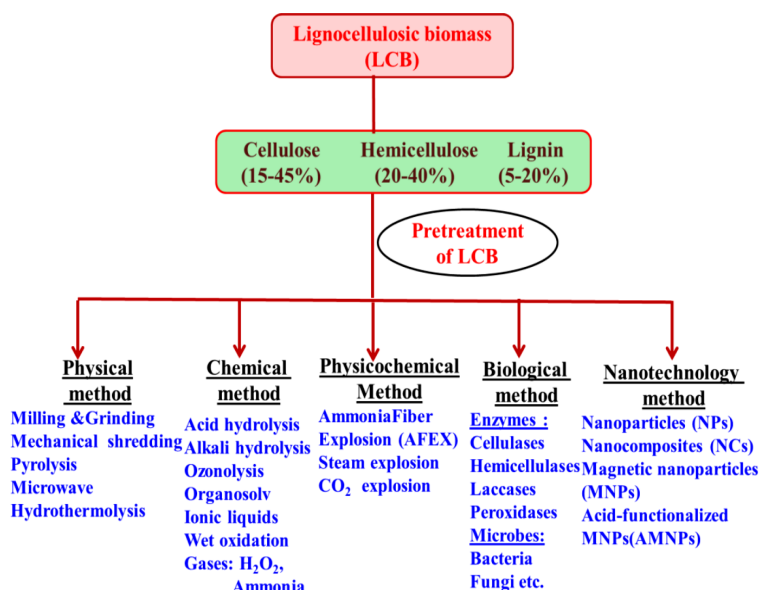


Figure 3. Shows the several pretreatment procedures involved in lignocellulosic breakdown (cullled from Singhvi et al. 2022 [pp. 3])

## PHYSICAL PRETREATMENT

The foremost aim of physical pretreatment is to shrink the biomass such that the cellulose component becomes accessible. The size reduction creates a wider surface area for enzyme attack, lowers the level of polymerization and consequently, gives rise to significant decrystallization of biomass.

## MECHANICAL DISRUPTION

To create smaller particles with a particular size distribution, the biomass has to be milled, hence mechanical disruption. Since biomass granulation enhances mass and heat transport, this reduction of size of particles is the primary step in this pretreatment technique [38]. The natural structure and crystallinity of biomass are altered by mechanical disruption involving milling, mincing, chopping, grinding and crushing. These steps make the biomass more vulnerable to cellulase attack. According to literature, particle sizes ranging between 0.2 mm - 2 mm or 10 mm - 30 mm react maximally [39]. Particle size varies as a result of different physical techniques. Due to the shear forces created when these mechanical disruptions take place, mass and heat transfer are equally reduced [39]. This method has a major challenge which is the ineffectiveness of milling in removing lignin. Lignin often prevents cellulase from accessing the cellulose part of the biomass by irreversibly binding to it. Hence, it is suggested that mechanical disruptions be used in conjunction with other pretreatment methods since it is not efficient as a stand-alone pretreatment method.

## EXTRUSION

To change the biomass's physical and chemical composition as it moves through the extruder, the biomass is heated up, mixed and then sheared. The fibrous structure of the biomass is disrupted by changes in screw speed and barrel temperature, which also shortens the fibers, making cellulose more accessible to cellulases and causing a break down in the biomass structure. In the study done by [51] Switch grass was pre-treated at screw speed (200 rpm) and the barrel temperature (75°C) yielding 28.2% reducing sugars. After enzymatic hydrolysis, pretreatment of soybean hulls (humidity in barrel, 40% on a wet basis) at screw speed of 350rpm and temperature of 80°C led to 94.8% glucose conversion. High shear, high agitation rate, moderate and suitable barrel temperature and brief residence times are the benefits of this process.

According to Karunanithy and Muthukumarappan [41], extruder variables including barrel temperature, compression ratio, and screw speed significantly impacted sugar recovery. They used maize cob as their substrate and carried out a pretreatment by altering different temperatures and screw speeds.

At percentages of 75, 49, and 61, glucose, xylose, and mixed sugar, respectively, were obtained. These

outcomes exceeded the control. In a similar vein, Karunanithy and Muthukumarappan [40] investigated the effects of cellulase combined with beta glucosidase in the ratio of 1:1 and 1:4 on sugar yield from specific warm season grasses like prairie cord grass, big bluestem, and switch grass at barrel temperatures of 50, 75, 100, 150, and 200 °C. The grasses produced the highest percentages of combined sugar output, 49.2, 66.2, and 28.2, respectively. The characteristics of the biomass material had a sizable impact on sugar recovery rates as well.

## ULTRASOUND

Small cavitation bubbles created during this approach assist in carbohydrate separation and depolymerization, breaking down biomass and improving cellulases' accessibility to cellulose. As a result, cellulose is more thoroughly saccharified after receiving ultrasonic pretreatment. During this pretreatment, LBM is subjected to ultrasound in a 10KHz to 20MHz frequency range; this alters the LBM's anatomical structure and causes both chemical and physical effects [60]. The targets are the hydroxyl groups on the phenolic rings of lignin-like compounds. This encourages the scission of the bond between hemicellulose and lignin. The efficiency of this method is greatly influenced by a number of important factors, including frequency, power, ultrasonic mode (continuous or pulsed), temperature solvent in use, aeration, reactor design and reactor configuration. These help biomass content removal and make up crucial variables that affect how well this method works. It has been demonstrated that biomass with smaller particle size responds more favorably to ultrasonic pretreatment than biomass with larger sizes. Sonication of corn starch slurry for 40 seconds produced a sugar volume 5-6 times above that of the control [60]. Seeing that cost of sonication is on the high side, opportunities to enhance this process by combining ultrasound method with techniques such as addition of oxidizers, peroxides and ozone should be considered.

## CHEMICAL PRETREATMENT

Chemical pretreatment methods are used most at times for lignin breakdown when compared biological or physical pretreatment usage; this is usually due to the fact that they are more effective and impact greatly on the biodegradation of complicated materials.

## ORGANOSOLV PRETREATMENT

This approach is best for biomass with high lignin content because lignin can be successfully liquefied by organic solvents [59]. In this technique, an organic solvent is used to process the biomass. To make the process more productive, base catalysts or inorganic/organic acids (such as Hydrochloric acid,

sulfuric acid, and organic acids like acetyl salicylic acid, salicylic acid, oxalic acid) are added. The materials are then recycled and reused by distillation [86]. When the pretreatment is carried out in the absence of a catalyst, temperatures within the range of 180°C - 210°C are most suitable. On the other hand, the addition of a catalyst enables the reaction to take place at lower temperatures like below 175°C. The approach is such that the pretreatment of biomass is preceded with washing using an organic solvent either, ethanol or methanol, this prevents dissolved lignin from precipitating and then water. The organic solvent is allowed to evaporate and condense before the organic material is released. The solvent can also be recycled.

As a result, three distinct fractions, aqueous solution made up of dry lignin, hemicellulose fraction and pure cellulose, are obtained from the organosolv pretreatment. This procedure has many benefits. During the procedure, pure lignin and reasonably pure cellulose are created. Due to the low boiling points of ethanol and methanol, solvent can be easily recovered by distillation [9]. Zhang *et al.* [94] used methanol/dioxane binary solvent with microwave irradiation at 120°C for 10 minutes on biomass material. 99% conversion of enzymatic saccharification was achieved. Amiri *et al.* [3] pre-treated rice straw with 1% sulfuric acid in 75% ethanol aqueous solution at 150°C for 60 minutes. The enzymatic sugar concentration stood at a high volume of 31g/L. There are many disadvantages to this approach as well; organic solvents are expensive, using volatile organic liquids at high temperatures necessitates the use of specially designed containers to avert leaks and fires. Other drawbacks include the cost of recycling that might endanger enzymatic hydrolysis and fermenting organisms [79].

#### PRETREATMENT WITH DILUTE ACID

One of the most developed technologies in use is the pretreatment of biomass with diluted acids. The hemicellulose in biomass can be thoroughly solubilized in this pretreatment type by diluted acids like sulfuric acids, resulting in biomass that can be hydrolyzed more easily [25, 67]. There have been studies showing the effectiveness of using acids as a pretreatment option. Some drawbacks of pretreating with dilute acid include the generation of microbial inhibitors from sugar disintegration at high conditions and retention of cellulose crystallinity [74]. High solids loading, being the proportion of biomass solids in the pretreatment mixture, is another crucial element in the acid pretreatment process. Certain catalysts have equally demonstrated their value in enhancing pretreatment impact on biomass. Targeting lignin and disabling the lignin-carbohydrate network are the major steps in this mechanism. Sulfite pretreatment is another choice for LBMs because, in this technique, diverse measures of sulfite or bisulphite solution are used. When applied at different pH levels, hemicellulose and lignin are better

eliminated to speed up the enzyme hydrolysis of cellulose [31]. Risanto *et al.* [71] conducted a study on the effectiveness of various dilute organic acid pretreatments of sugarcane bagasse and oil palm empty fruit bunch fiber. The outcomes showed that among other organic acids, pretreatment with maleic acid produces the highest levels of xylose and glucose release. Further research was done on the effects of heating temperature, heating time, and concentration. Its viability as a sulfuric acid substitute was dependent on a pretreatment of diluted maleic acid at a rate of 1% (w/w) at 180 °C.

Furthermore, after pretreatment, maleic acid did not appear to strongly promote the synthesis of either furfural or 5-HMF in the liquid hydrolysate. Wi *et al.* [90] came up with hydrogen-peroxide- acetic acid pretreatment (HPAC) to get rid of lignin without the use of intense temperatures or potent acids. The production of fermentation inhibitors during the process are eliminated while the enzyme loading is reduced when using this method on various lignocellulosic materials. According to their research, HPAC performed best under 80°C for two hours with a 50/50 mixture of H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH. The recovered solid's composition after the HPAC pretreatment was 74% cellulose, 20% hemicellulose and 0.9% lignin. HPAC successfully removed lignin worth 97.2% [90].

#### ALKALINE PRETREATMENT

During alkaline pretreatment, saponification and solvation, two significant reaction mechanisms take place. The internal surface area of the lignocellulosic cell increases as a result of solvation. On the other hand, when the uronic acid ester bond (4-O-methyl-D-glucuronic acid) connected to the xylan skeleton is saponified, an alkaline agent produces a charged carboxyl group. Additionally, it breaks down lignin-hemicellulose bonds, which ultimately cause the cellulose, hemicellulose and lignin matrix to be disrupted. Due to the absence of binding bonds, the lignocellulose pore structure is enlarged, making the lignocellulose constituents readily accessible for enzymatic and microbial action and breakdown. Switch grass, rice straw, sugarcane bagasse, sugar cane ear, dendro-calamus, maize stalk, cottonwood and other LBMs have all been subjected to this pretreatment. Lime, NaOH and Ca(OH)<sub>2</sub>, are the regular primary substances used in alkaline pretreatment [15]. In a study carried out by [4], 2% NaOH was used at 121°C for 10 minutes for enzymatic hydrolysis. 46.7% and 55.3% were the levels of glucose content and enzymatic hydrolysis respectively. The set ups bounced to 2.4-2.5 times more than the untreated after treatment with NaOH. Jiang *et al.* [35] deliberated on the pretreatment of giant reeds using NaOH and Ca(OH)<sub>2</sub>. Sugar turnover were 85% and 70% more than the production from the untreated giant reeds. Use of diluted NaOH has been proven to be effective on stems with lignin levels between 10%-18%. It has been

discovered that it has no impact on softwoods with a lignin contents more than 26%, though. Wang *et al.* [88] experimented using ozone-NaOH as a joint pretreatment for corn stover. This combination removed 84.4% lignin. Dai *et al.* [20] adopted a combination method which used bacteria with NaOH-urea, to help enhance the enzymatic hydrolysis action on rice straw. This pretreatment increased the supply of reducing sugar and glucose by 1.40 and 1.37 respectively. Alkaline pretreatment typically involves less sugar decomposition than acid pretreatment, because it is carried out at lower pressures and temperatures than acid and steam explosion pretreatments. As a result, less energy is used during alkaline pretreatment. When carried out in ambient conditions, alkaline pretreatment is typically laborious. Another drawback is the loss of alkalinity caused by the incorporation of salts into the biomass, which makes it impossible to recover them.

## OZONOLYSIS

This method includes using oxidizing substances like Ozone gas to lower the amount of lignin in biomass thereby enhancing enzymatic hydrolysis. When choosing whether to pretreat biomass with ozone gas, biomass moisture content is a crucial consideration. This is due to the fact that lignin's oxidation potential is inversely correlated with its water content. Many LBMs like poplar sawdust, bagasse, peanuts, cotton straw, pine, wheat straw have been used to study this method. The fact that this process typically operates at room temperature and pressure makes it appealing. However, industrial-level applications are faced with the problem of acquiring large amounts of ozone for pretreatment. This method does not produce inhibitory compounds that interfere with subsequent reactions such as hydrolysis and fermentation. Studies are being done to create ozone concentrations that can be used industrially and for commercial purposes [51].

## PHYSICO-CHEMICAL PRETREATMENT

This category of pretreatment merges chemical and physical procedures. Together, they disintegrate hemicellulose and change the lignin's make-up to make the cellulose accessible.

## STEAM EXPLOSION

This is a pretreatment system that occurs at intense temperature and pressure; both chemical and mechanical forces are involved in this pretreatment [24, 92]. Because particle size, temperature and residence time have an impact on steam explosion efficiency, careful steam explosion optimization is necessary. The main inhibitors made are weak acids, phenolic compounds and furan derivatives (HMF and furfural coming from the decomposition of hexoses and pentoses). The high temperature also causes lignin to

go through chemical changes, which cause it to be redistributed and redeposited as lignin droplets. The enzymatic hydrolysis is adversely affected by this "pseudo-lignin"; however, at lower temperatures, partial breakdown of the lignin-carbohydrate matrix can result in soluble lignin components condensing or precipitating, creating indigestible biomass. As a result, temperature is a crucial process factor that needs to be optimized carefully. The steam explosion process has some unique characteristics when likened to other pretreatment methods. For instance, the process provides nearly complete sugar recovery, requires fewer chemicals and conditions (aside from softwoods, which require acid catalysis), has low recycling costs and has minimal environmental impact. Use of large particle sizes in the biomass is possible.

Borand *et al.* [11] used demonstrated steam explosion treatment at 190°C for 10 minutes using pine. 97.7% was the final yield of glucose produced while 85.6%, 87.8%, 86.4%, 90.3% were yields of xylose, mannose, galactose and arabinose respectively.

## AMMONIA PRETREATMENT

Ammonia is used to pretreat biomass through the Fiber/Freeze Explosion (AFEX) or Aqueous Ammonia Soaking (SAA) processes. Typically, a 5-15% ammonia solution is passed through the biomass for the liquid phase pretreatment at 150°C -180°C. The solution in the reactor can be recovered when the volumetric flow rate of ammonia is 1-5 mL/min and retention time 10-90 min. The lignin is depolymerized and solubilized by the aqueous ammonia reaction, which enhances enzymatic hydrolysis [37]. The accessibility of cellulose to cellulases is thus affected by a blend of physical and chemical changes, significantly raising the susceptibility of pre-treated LBM to subsequent enzymatic hydrolysis. Krishnan *et al.* [50] used AFEX on bagasse and it resulted in the production of 85% cellulose and 95-98% xylan. Kim and Day, [47] used AFEX on various LBM ranging from switch grass to ryegrass straw; 80% sugar was released in the presence of ammonia and water, ratio 1:1 at 90°C.

## BIOLOGICAL PRETREATMENT

To enhance the availability of LBM for enzymatic hydrolysis, bacteria and fungi are used. Lignin, hemicellulose and some cellulose are primarily broken down by white rot, soft rot and brown fungi. Brown rot basically targets lignin, whereas white rot and soft rot targets cellulose and lignin by nature. White rot fungi possess the ability to degrade lignin because of the presence lignin-degrading enzymes peroxidase and laccase [5, 23].

White rot fungi have been discovered to be the most efficient of all the fungi. Different species of white rot fungi, such as *Pleurotus ostreatus*, *Phanerochaete chrysosporium*, *Ceriporiopsis*

*subvermispora*, *Cyathus stercoreus*, *Pycnoporus cinnabarinus* and *Ceriporia lacerata* have been studied in different biomass. Biological pretreatment differs from other processes in that it uses little energy and produces no toxic byproducts, even though hydrolysis takes longer. Industrial applications are typically not possible due to the requirement to continuously monitor microbial growth. For the process to be improved in the future, the best strain and culture conditions should be used for the pretreatment (table 2).

**PRETREATMENT VIA NANOTECHNOLOGY**

Utilizing nanoparticles can result in the catalytic processing of lignocellulosic materials. Since they can be used often and on for repeated cycles, magnetic nanoparticles (MNP) are been used frequently for the pretreatment of LBM materials. The lower the overall cost of the process. Because of their small size, nanoparticles interact with biomass to produce fermentable sugars by entering the cell with all of the LBM materials [2]. MPN's are highly magnetic and can be used repeatedly in a variety of applications. In a recent study, the impact of magnetic iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles on enhanced biogas production and LBM pretreatment was investigated. The set up demonstrated that the presence of Fe<sub>3</sub>O<sub>4</sub> MNP's significantly

improved the generation of biogas [43]. Several new methods have also emerged as favorable sustainable pretreatment answers for the extensive pretreatment of lignocellulosic biomass [56, 84]. When compared to the control, pretreatment of wheat straw with perfluoroalkylsulfonic and alkylsulfonic acid-functionalized NPs released about 31% higher sugar concentration [64]. By using enzymes and other biocatalyst immobilized on MNPs, nanobiocatalysis is currently improving the field of nanotechnology. The catalytic efficiency of enzyme maybe improved by using this technique [70, 76].

**IONIC LIQUIDS PRETREATMENT (ILS)**

The search for kinder, more environmentally friendly pretreatment agents has increased due to drawbacks associated with chemical-physical pretreatment techniques. No pretreatment technology is successful due to the wide variety of LBM compositions and compositions, but ILs are emerging as green solvents that deal with the concerns of environmental safety and pretreatment economics [8]. ILs are a relatively new method of pre-treating biomass which dissolves and pretreats lignocellulosic biomass using molten salts at room temperature (Fig. 4).

Table 2. Shows the different pretreatment methods, their benefits and limitations

Pretreatment procedures	Benefits	Limitations	References
Mechanical disruption	Reduces cellulose crystallinity and particle size	High power consumption is needed when compared to inherent biomass energy.	[91]
Extrusion	Low price and greater monitoring and control of the whole process. It can easily adjust to changes in various processes.	Ample force is required and set up cost is usually much.	[96]
Steam Explosion	Damages the pattern and arrangement and breaks down hemicellulose thereby raising the conversion efficiency and enzymatic hydrolysis. Lignin component is also changed; it is equally cost effective.	An incomplete lignin-carbohydrate breakdown and partial destruction of the xylan fraction.	[11, 92]
AFEX	Increases the amount of surface that is accessible; partially takes away lignin and hemicellulose and does not create any inhibitors.	Inefficient for biomass that contains a lot of lignin.	[52, 80]
Ozonolysis	lowers the content of lignin; does not produce threatening residues.	This process is expensive and large amounts of Ozone are needed.	[51]
Organosolv	Hydrolyzes lignin and hemicelluloses	It is necessary to drain, evaporate and recycle solvents from the bioreactor; also, the cost of operation is high.	[79]
Biological	Breaks down lignin and hemicellulose and requires lower energy requirements.	Hydrolysis occurs at a very slow rate. Hence taking long processing time.	[16, 75]

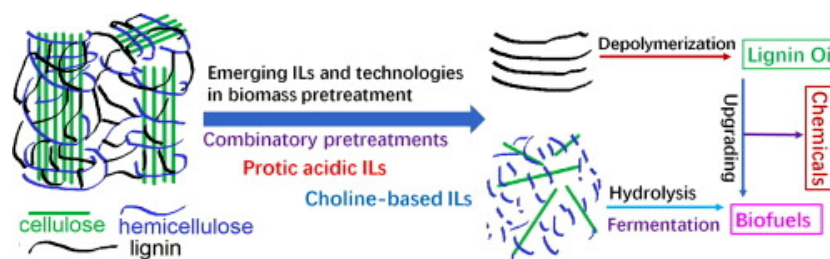


Figure 4. Shows ionic liquid pretreatment of biomass (culled from Zhang *et al.* 2021 [pp. 124522])

Ionic liquids are not restricted in terms of biodegradability, toxicity, hydrophobicity, viscosity, electrochemical stability or thermal stability. Examples include 1-n-butyl-3-methylimidazolium chloride (BMIMCl) and 3-methyl-N-butylpyridinium chloride have been disclosed to have cellulose solubilities of 25% and 39% respectively [19]. Nguyen *et al.* [64] studied the impact of ammonia together with ionic liquid, 1-Ethyl-3-methylimidazolium acetate. High recovery of cellulose (82%) and high glucose conversion (97%) from rice straw were the results of this. According to [64] the great effect was because of the ILs which increased the porosity of the biomass making it more prone to cellulases [8]. In terms of sugar production and enzyme kinetics, ILs pretreatment has proven to be more effective than dilute acid technique [8, 53].

### HYDRODYNAMIC CAVITATION

Water molecules split into  $\text{OH}^\cdot$  and  $\text{H}^\cdot$  during the hydrodynamic cavitation process at high pressures and temperatures. The cavitation process generates more reactive  $\text{OH}^\cdot$  radicals that are crucial in the oxidation of lignin molecules. The performance of this pretreatment approach can be enhanced by the radicals that are formed [21]. In the hydrodynamic cavitation (HD) reactor, there are two ways to pre-treat biomass. A closed loop configuration is used in one method to pass the biomass multiple times. Another method feeds the HD zone multiple times by closed-loop circulation while using biomass slurry as the working fluid [48] (Fig. 5).

Several studies have demonstrated HD pretreatment in combination with other methods for enhanced removal of lignin. Kim *et al.* [45] demonstrated that the use of alkaline pretreatment of biomass in a single-orifice HD reactor produced better estimates of the process's energy requirements, a reduction in the biomass's lignin content, and an overall increase in the yields of biofuel. A combined method of HD and caustic pretreatment of sugarcane bagasse with a HD reactor equipped using an orifice plate was used by [27] to remove 60.4% of the lignin in 44.48 minutes. In 30

minutes, up to 51.52% lignin was removed according to a related study by Hilares *et al.* [28]. For the simultaneous saccharification and fermentation (SSF) process, sugarcane bagasse feedstock was pre-treated using a combination of alkali and HD pretreatment [29].

Nakashima *et al.* [63] carried out almost same research where HD was adopted alongside sodium percarbonate (SP) for lignocellulosic biomass pretreatment. The combined set up of HD-SP was compared to that of ultrasonication and SP (US-SP). These set up were rated by how of lignin they could remove and how much glucose and xylose would be formed. Fourier transform infrared spectra indicated that both set ups removed equal percentages of lignin, however in the case of glucose and xylose generation, the HD-SP set up performed better. The both systems did not generate any inhibitor. HD-SP set up proved to be most preferable for pretreatment of lignocellulosic biomass at industrial capacity [63]. The combination of HD and hydrogen peroxide pretreatment generated 95.4% cellulosic digestibility, while the joint pretreatment of NaOH-HD produced the most amount of ethanol ( $17.26 \text{ gL}^{-1}$ ) among the various catalysts used [30, 55].

The combination of HD and enzymatic methods on a biomass slurry containing water, biomass powder and enzyme, resulted in a high lignin removal of 47.4% [48]. Since HD allows for higher lignin removal, easy cellulose accessibility for saccharification, minimal energy consumption and simple construction and scaling, traditional methods are now outmoded and ineffective. Pretreatment's effectiveness is highly influenced by the current operating circumstance (such as substrate and temperature) and the microbial community's activity.

### DETOXIFICATION OF TOXIC INHIBITORS PRODUCED DURING PRETREATMENT PROCESSES

Lignocellulosic biomass materials usually generate a number of small molecular weight fermentation inhibitors while the hydrolysis process takes place [26, 49]. Inhibitors such as phenolic compounds, aliphatic

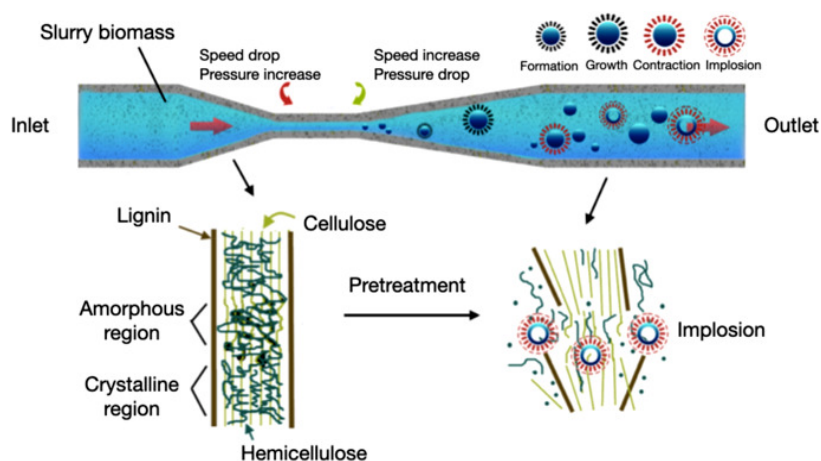


Figure 5. Shows biomass slurry as the working fluid in hydrodynamic cavitation (HD) reactor (culled from Bimestre *et al.* 2022 [pp. 6])



acids, furan aldehydes, iorganic ions and bioalcohol, are major constraints to fermentation and also seriously affect the use of substrates by micro-organisms. Production of toxic compounds must be minimized to the barest minimum since it can influence enzymatic hydrolysis and fermentation.

Making sure pretreatment techniques are economically viable and do not produce threatening substances or chemical compounds that obstruct the enzymatic and fermentation processes should be one of these solutions [9]. The main principle is that these inhibitors are formed when hemicellulose breaks down to 5-hydroxymethylfurfural (5-HMF) and fufural [17, 88]. Formic acid is produced with the breakdown of 5-HMF and fufural [14]. The presence of furan aldehydes and phenols interfere with enzymatic hydrolysis to stop microbial enzyme activity [33, 61]. As a remedy, phenols can be transformed to fewer threatening components by fermenting microbes or by utilizing special enzymes like laccases and peroxides which oxidize lignin [8] (table 3).

In addition to physical methods and the likes, using less recalcitrant biomass that produce little or no inhibitors' during pretreatment is advisable. Genetic metabolic engineering of selected microorganisms can equally act as a strategy to circumvent challenges with lignocellulosic-derived inhibitors formed during pretreatment [36]. Yeast strains have been engineered making them resistant to phenolic compounds and furan aldehyde.

A recent development in chemical detoxification is the ability to perform the treatment in situ in the bioreactor by using reducing agents such as sulfur oxyanions or sulfhydryl chemicals [1]. Cavka *et al.* [12] studied this approach. The findings were that the effect of reducing agents was because of sulfonation of inhibitors, which usually made them have little tendency to react chemically but able to dissolve in water.

## CONCLUSION

Today, it is crucial to figure out how to increase the overall yield of the valuable substances that make up lignocellulosic materials. It would be ideal to have a pretreatment technique that effectively recovers lignin and carbohydrates. But it all depends on the circumstances, the process and the outcome. Today, it is crucial to find ways to increase the overall yield of the valuable components that make up lignocellulosic biomass materials. Energy requirements in production processes, must always be satisfied by the internal or external integration of high energy streams, such as in pulp mills where surplus lignin serves as the process' primary energy source. Pretreatment is one of the key initial steps if one want access raw resources more conveniently. It is difficult to pin down the "best" pretreatment for all conditions and substrates but it is important that some necessary conditions of pretreatment processes are met. Pretreatment has clear targets like lignin degradation, destruction of cellulose crystallinity, improve the digestibility of cellulose and lignocellulose porosity increase. Besides this, the pretreatment must adhere to certain standards like cellulose digestibility. The cellulose in plant fibers needs to be pretreated with acids or microbial enzymes in order to be broken down into its component sugars. A low-cost pretreatment strategy should be effective. This is accomplished by limiting the use of expensive materials at all times [9]. Energy demand should be kept to a minimum because pretreatment consumes a lot of energy. This paper focused on pretreatment techniques, their mechanisms, and the integration and prospects of different pretreatment technologies of lignocellulosic biomass and x-rayed how they can effectively treat organic waste, meet local energy demand, cut down on waste, and boost energy security.

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**Table 3.** Shows standard detoxification techniques and their merits and demerits

Pretreatment technique	Detoxification technique	Merit	Demerit	Reference
Physical technique	Adsorption, membrane filtration and extraction	Most inhibitors can be removed.	Much sugar is lost using this technique.	[42]
Chemical technique	Reducing agent and persulfate method	Weak acids are removed.	Large volumes of reagents are needed and might not be recovered when the process is over.	[97]
Biological	Enzyme consortia	There is low loss of sugar and conditions are mild.	Much time is required for this approach. The reaction is usually long.	[73]
Integrated approach	Activated carbon and CaO, ion exchange resin	Has a powerful removal speed and it is highly specific	Cost is high	[16]

## REFERENCES

- [1] Alriksson, B., Cavka, A., Jönsson, L.J., (2011): Improving the fermentability of enzymatic hydrolysates of lignocellulose through chemical in-situ detoxification with reducing agents. *Bioresource Technology*, 102: 1254-1263.
- [2] Amin, F.R., Khalid, H., Zhang, H., Rahman, S., Zhang, R., Liu, G., Chen, C., (2017): Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express*, 7: 72.
- [3] Amiri, H., Karimi, K., Zilouei, H., (2014): Oragnosolv pretreatment of rice straw for efficient acetone, butanol and ethanol production. *Bioresource Technology*, 152: 450-456.
- [4] An, H., Lee, K.H., Jang, Y.W., Kim, C., Yoo, H.Y., (2021): Improved glucose recovery from *Sicyos angulatus* by NaOH Pretreatment and application to Bioethanol production. *Processes*, 9(2): 245.
- [5] Anu, K.A., Rapoport, A., Kunze, G., Kumar, S., Singh, D., Singh, B., (2020): Multifarious pretreatment strategies for the lignocellulosic substrates for the generation of renewable and sustainable biofuels: A review. *Renewable Energy*, 160: 1228-1252.
- [6] Anukam, A., Mamphewli, S., Reddy, P., Meyer, E., Okoh, O., (2016): Pre-processing of sugarcane bagasse for gasification in a downdraft biomass gasifier system: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 66: 775-801.
- [7] Anukam, A.I., Berhel, J., Frodeson, S., Famewo, E.B., Nyamukamba, P., (2019): Characterization of pure and blended pellets made from Norway spruce and pea starch: A comparative study of bonding mechanism relevant to quality. *Energies*, 12(23): 1-22.
- [8] Bhatt, S.M., Shilpa, (2014): Lignocellulosic feedstock conversion, inhibitor detoxification and cellulosic hydrolysis—a review. *Biofuels*, 5(6): 633-649.
- [9] Bhutto, A.W., Qureshi, K., Harijan, K., Abro, R., Abbas, T., Bazmi, A.A., Karim, S., Yu, G., (2017): Insight into progress in pre-treatment of lignocellulosic biomass. *Energy*, 122: 724–745.
- [10] Bimestre, T.A., Junior, J.A.M., Canttieri, E.V., Tuna, C.E., (2022): Hydrocavitation for lignocellulosic biomass pretreatment: a review of recent developments and future perspectives. *Bioresource and Bioprocessing*, 9(7): 6
- [11] Borand, M.N., Isler, K.A., Karaosmanoglu, F., (2020): Saccharification yield through enzymatic hydrolysis of the steam-exploded pinewood. *Energies*, 13: 4552-4552.
- [12] Cavka, A., Alriksson, B., Ahnlund, M., Jönsson, L.J., (2011): Effect of sulfur oxyanions on lignocellulose-derived fermentation inhibitors. *Biotechnology and Bioengineering*, 108: 2592–2599.
- [13] Cheah, W.Y., Sankaran, R., Loke, P.S., Ibrahim, T., Baizura, T.N., Wayne, K., (2020): Pretreatment methods for lignocellulosic biofuels production: current advances, challenges and future prospects. *Biofuel Research Journal*, 7(1): 1115-1127.
- [14] Chen, H.Q., Li, J., Wan, C., Fang, Q., Bai, F.W., Zhao, X.Q., (2019): Improvement of inhibitor tolerance in *Saccharomyces cerevisiae* by over expression of the quinone oxidoreductase family gene, YCR102C. *FEMS Yeast Research*, 19: 55-67.
- [15] Chen, B.Y., Chen, S.W., Wang, H.T., (2012): Use of different alkaline pretreatments and enzyme models to improve low-cost cellulosic biomass conversion. *Biomass and Bioenergy*, 39: 182-191.
- [16] Cheng, Z., Yang, R.D., Liu, X., Liu, X., Chen, H., (2017): Green synthesis of bacterial cellulose via acetic acid pre-hydrolysis liquor of agricultural corn stalk used as carbon source. *Bioresource Technology*, 234: 8-14.
- [17] Cola, P., Procopio, D.P., Tabosa de Castro Alves, A., Rebelo Carnevalli, L., Viana Sampaio, I., Labate Vale da Costa, B., Olitta Basso, T., (2020): Differential effects of major inhibitory compounds from sugarcane-based lignocellulosic hydrolysates on the physiology of yeast strains and lactic acid bacteria. *Biotechnology Letters*, 42: 571-582.
- [18] Collard, F.-X., Blin, J., (2014): A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable and Sustainable Energy Reviews*, 38: 594-608.
- [19] Dadi, A.P., Schal, C.A., Varanasi, S., (2007): Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. *Applied Biochemistry and Biotechnology*, 137: 407-421.
- [20] Dai, Y.Z., Si Meng, Y., Chen, Y.H., Zhang, N.L., Zhou, M., Liao, Q., Shi, D.Q., Liu, Y., (2015): Combination of biological pretreatment with NaOH/Urea pretreatment at cold temperature to enhance enzymatic hydrolysis of rice straw. *Bioresource Technology*, 198: 725-731.
- [21] Desikan, R., Thangavelu, K., Uthandi, S., (2019): Hydrodynamic cavitation – A promising technology for biomass pretreatment. *International Journal of Environmental Science and Natural Resources*, 19(2): 556015.
- [22] deSouza, A.P., Leite, D.C., Pattathil, S., Hahn, M.G., Buckeridge, M.S., (2013): Composition and structure of sugarcane cell wall polysaccharides: implications for second-generation bioethanol production. *BioEnergy Research*, 6(2): 564-579.
- [23] Dey, N., Kumar, G., Vickram, A.S., Mohan, M., Singhanian, R.R., Patel, A.K., (2022): Nanotechnology-assisted production of value added biopotential energy-yielding products from lignocellulosic biomass refinery - A review. *Bioresources Technology*, 344: 126-171.
- [24] Ewanick, S., Bura, R., (2011): The effect of biomass moisture content on bioethanol yields from steam pretreated switch grass and sugarcane bagasse. *Bioresource Technology*, 102: 2651-2658.
- [25] Foston, M.B., Ragauskas, A.J., (2010): Changes in lignocellulosic supramolecular and ultrastructure during dilute acid pretreatment of Poplar and switchgrass. *Biomass Bioenergy*, 34: 1885-1895.
- [26] Hidayatullah, I.M., Setiadi, T., Kresnowati, M.T.A., Boopathy, R., (2020): Xylanase inhibition by the derivatives of lignocellulosic material. *Bioresource Technology*, 300: 122740.
- [27] Hilares, R.T., Dos Santos, J.C., Ahmed, M.A., Jeon, S.H., da Silv, S.S., Han, J.I., (2016): Hydrodynamic cavitation-assisted alkaline pretreatment as a new approach for sugarcane bagasse biorefineries. *Bioresource Technology*, 214: 609-614.
- [28] Hilares, R.T., de Almeida, G.F., Ahmed, M.A., Antunes, F.A., da Silva, S.S., Han, J.I., Dos Santos, J.C., (2017a): Hydrodynamic cavitation as an efficient pretreatment method for lignocellulosic biomass: A parametric study. *Bioresource Technology*, 235: 301-308.
- [29] Hilares, R.T., Ienny, J.V., Marcelino, P.F., Ahmed, M.A., Antunes, F.A., da Silva, S.S., Dos Santos, J.C., (2017b): Ethanol production in a simultaneous saccharification and fermentation process with interconnected reactors employing hydrodynamic

- cavitation-pretreated sugarcane bagasse as raw material. *Bioresource Technology*, 243: 652-659.
- [30] Hilares, R.T., Kamoie, D.V., Ahmed, M.A., da Silva, S.S., Han, J.I., Dos Santos, J.C., (2018): A new approach for bioethanol production from sugarcane bagasse using hydrodynamic cavitation assisted-pretreatment and column reactors. *Ultrasonics Sonochemistry*, 43: 219-226.
- [31] Huang, C., Li, R., Tang, W., Zheng, Y., Meng, X., (2022): Improve enzymatic hydrolysis of lignocellulosic biomass by modifying lignin structure via sulfite pretreatment and using lignin blockers. *Fermentation*, 8(10): 558.
- [32] Imman, S., Arnthong, J. Burapatana, V., Champreda, V., Laosiripojana, N., (2015): Fractionation of rice straw by a single-step solvothermal process: Effects of solvents, acid promoters and microwave treatment. *Renewable Energy*, 83: 663-673.
- [33] Iwaki, A., Kawai, T., Yamamoto, Y., Izawa, S., (2013): Biomass conversion inhibitors furfural and 5-hydroxymethylfurfural induce formation of messenger RNP granules and attenuate translation activity in *Saccharomyces cerevisiae*. *Applied and Environmental Microbiology*, 79: 1661-1667.
- [34] Jaramillo, I., Sanchez, A., (2018): Mass flow dynamic modeling and residence time control of a continuous tubular reactor for biomass pretreatment. *ACS Sustainable Chemistry & Engineering*, 6(7): 8570-8577.
- [35] Jiang, D.P., Xu, M.G., Tian, Z., Zhou, C., Zhi, P.Z., Chao, H., Quan, G.Z., Ye, B.L., (2020): Effect of alkaline pretreatment on photo-fermentative hydrogen production from giant reed: comparison of NaOH and Ca(OH)<sub>2</sub>. *Bioresource Technology*, 30: 497-107.
- [36] Jönsson, L.J., Alriksson, B., Nilvebrant, N.O., (2013): Bioconversion of lignocellulose: inhibitors and detoxification. *Biotechnology for biofuels*, 6(1): 1-10.
- [37] Jung, H., Yoon, H.G., Park, W., Choi, C., Wilson, D.B., Shin, D.H., Kim, Y.J., (2007): Effect of sodium hydroxide treatment of bacterial cellulose on cellulase activity. *Cellulose*, 15: 465-471.
- [38] Kamarudin, S., Jainal, M., Aziz, A., Mohd, S., Nor, S., Mohamad, D., Ahmad, R., (2014): Mechanical pretreatment of lignocellulosic biomass for biofuel production. *Applied Mechanics and Materials*, 625: 838-841.
- [39] Kapoor, M., Semwal, S., Gaur, R., Kumar, R., Gupta, R.P., Puri, S.K., (2018): The pretreatment technologies for deconstruction of lignocellulosic biomass. In: Singhania, R., Agarwal, R., Kumar, R., Sukumaran, R. (eds) *Waste to Wealth. Energy, Environment, and Sustainability*. Springer, Singapore, pp. 395-421.
- [40] Karunanithy, C., Muthukumarappan, K., (2010): Influence of extruder temperature and screw speed on pretreatment of corn stover while varying enzymes and their ratios. *Applied Biochemistry and Biotechnology*, 162: 264-279.
- [41] Karunanithy, C., Muthukumarappan, K., (2010): Effect of extruder parameters and moisture content of switchgrass, prairie cord grass on sugar recovery from enzymatic hydrolysis. *Applied Biochemistry and Biotechnology*, 162: 1785-1803.
- [42] Keshav, P.K., Shaik, N., Koti, S., Venkateswar, R.L., (2016): Bioconversion of alkali delignified cotton stalk using two stage dilute acid hydrolysis and fermentation of detoxified hydrolysate into ethanol. *Industrial Crops and Products*, 91: 323-331.
- [43] Khalid, M.J., Waqas, A., Nawaz, I., (2015): Synergistic effect of alkaline pretreatment and magnetite nanoparticle application on biogas production from rice straw. *Bioresources Technology*, 275: 288-296.
- [44] Khan, M.U., Usman, M., Ashraf, M.A., Dutta, N., Luo, G., Zhang, S., (2022): A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas: Opportunities and Limitations. *Chemical Engineering Journal Advances*, 10: 100263.
- [45] Kim, I., Lee, I., Jeon, S.H., Hwang, T., Han, J.I., (2015). Hydrodynamic cavitation as a novel pretreatment approach for bioethanol production from reed. *Bioresource Technology*, 192: 335-339.
- [46] Kim, S., Dale, B.E., (2004): Global potential bioethanol production from wasted crops and crop residues. *Biomass and Bioenergy*, 26: 361-375.
- [47] Kim, M., Day, D.F., (2011): Composition of sugar cane, energy cane, and sweet sorghum suitable for ethanol production at Louisiana sugar mills. *Journal of Industrial Microbiology and Biotechnology*, 38(7): 803-807.
- [48] Kiruthika, T., Ramesh, D., Taran, O.P., Sivakumar, U., (2018): Delignification of corncob via combined hydrodynamic cavitation and enzymatic pretreatment: process optimization by response surface methodology. *Biotechnology Biofuels*, 11(1): 203.
- [49] Klinke, H.B., Olsson, L., Thomsen, A.B., Ahring, B.K., (2003): Potential inhibitors from wet oxidation of wheat straw and their effect on ethanol production of *Saccharomyces cerevisiae*: wet oxidation and fermentation by yeast. *Biotechnology Bioengineering*, 81(6): 738-747.
- [50] Krishnan, C., da Costa Sousa, L., Jin, M., Chang, L., Dale, B.E., Balan, V., (2010): Alkali-based AFEX pretreatment for the conversion of sugarcane bagasse and cane leaf residues to ethanol. *Biotechnology Bioengineering*, 107: 441-450.
- [51] Kumar, A.K., Sharma, S., (2017): Recent updates on different methods of pretreatment of lignocellulosic feedstocks: A review. *Bioresources and Bioprocessing*, 4(1): 1-19.
- [52] Lau, M.W., Dale, B.E., (2016): Effect of primary degradation reaction products from Ammonia Fiber Expansion (AFEX)-treated corn stover on the growth and fermentation of *Escherichia coli* K011. *Bioresource Technology*, 101(20): 7849-7855.
- [53] Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H.V., Auer, M., Vogel, K.P., Simmons, B.A., Singh, S., (2010): Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification. *Bioresource Technology*, 101(13): 4900-4906.
- [54] Łukajtis, R., Kucharska, K., Hołowacz, I., Rybarczyk, P., Wychodnik, K., Słupek, E., Kamiński, M., (2018). Comparison and optimization of saccharification conditions of alkaline pre-treated triticale straw for acid and enzymatic hydrolysis followed by ethanol fermentation. *Energies*, 11(3): 639.
- [55] Madison, M.J., Coward-Kelly, G., Liang, C., Karim, M.N., Falls, M., (2017): Mechanical pretreatment of biomass—Part I: Acoustic and hydrodynamic cavitation. *Biomass Bioenergy*, 98: 135-141.
- [56] Mahmood, H., Moniruzzaman, M., Iqbal, T., Khan, M. J., (2019): Recent advances in the pretreatment of lignocellulosic biomass for biofuels and value-added products. *Current Opinion in Green and Sustainable Chemistry*, 20: 18-24.

- [57] Meng, X., Pu, Y., Yoo, C.G., Li, M., Bali, G., Park, D.Y., (2017): An in-depth understanding of biomass recalcitrance using natural poplar variants as the feedstock. *ChemSusChem*, 10(1): 139-150.
- [58] Merklein, K., Fong, S.S., Deng, Y., (2016): Biomass utilization. In *Biotechnology for biofuel production and optimization*. Elsevier, pp. 291-324.
- [59] Mesa, L., Gonzalez, E., Cara, C., Gonzalez, M., Castro, E., Musatto, S.I., (2011): The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse. *Chemical Engineering Journal*, 168: 1157-1162.
- [60] Montalbo, L.M., Johnson, L., Khanal, S.K., Leeuwne, J.V., Grewell, D., (2010): Sonication of sugary-2 corn: a potential pretreatment to enhance sugar release. *Bioresources Technology*, 101: 351-358.
- [61] Moreno, A.D., Ibarra, D., Fernandez, J.L., Ballesteros, M., (2012): Different laccase detoxification strategies for ethanol production from lignocellulosic biomass by the thermotolerant yeast *Kluyveromyces marxianus* CECT 10875. *Bioresource Technology*, 106: 1-9.
- [62] Mori, T., Tsuobi, Y., Ishida, N., Nishikubo, N., Demura, T., Kikuchi, J., (2015): Multidimensional high-resolution magic angle spinning and solution-state NMR characterization of <sup>13</sup>C-labelled plant metabolites and lignocellulosic. *Scientific Reports*, 5: 11848.
- [63] Nakashima, K., Ebi, Y., Shibasaki-Kitakawa, N., Soyama, H., Yonemoto, T., (2016): Hydrodynamic cavitation reactor for efficient pretreatment of lignocellulosic biomass. *Industrial Engineering Chemical Resource*, 55(7): 1866-1871.
- [64] Nguyen, T.A.D., Kim K.R., Han S.J., Cho, H.Y., Kim, J.W., Park, S.M., Park, J.C., Sim, S.J., (2010): Pretreatment of rice straw with ammonia and ionic liquid for lignocellulosic conversion to fermentable sugars. *Bioresources Technology*, 101: 7432-7438.
- [65] Niju, S., Swathika, M., Balajii, M., (2020): Pretreatment of lignocellulosic sugarcane leaves and tops for bioethanol production. In *Lignocellulosic biomass to liquid biofuels*. Academic Press, pp. 301-324.
- [66] Pena, L., Ikenberry, M., Hohn, K.L., Wang, D., (2012): Acid-functionalized nanoparticles for pretreatment of wheat straw. *Journal of Biomaterials and Nanobiotechnology*, 3: 342.
- [67] Pierre Louis, A.M., Yu, H., Shumlas, S.L., Van Aken, B., Schoonen, M.A., Strongin, D.R., (2015): Effect of phospholipid on pyrite oxidation and microbial communities under simulated acid mine drainage (AMD) conditions. *Environmental Science & Technology*, 49(13): 7701-7708.
- [68] Prasad, A., Sotenko, M., Blenkinsopp, T., Coles, S.R., (2016): Life cycle assessment of lignocellulosic biomass pretreatment methods in biofuel production. *The International Journal of life Cycle Assessment*, 21: 44-50.
- [69] Qian, E.W., (2014): Pretreatment and saccharification of lignocellulosic biomass. In: Tojo, S., Hirasawa, T., (eds). *Research Approaches to Sustainable Biomass Systems*. Academic Press, pp. 181-204.
- [70] Rai, M., Ingle, A.P., Gaikwad, S., Dussan, K.J., da Silva, S.S., (2017): Role of nanoparticles in enzymatic hydrolysis of lignocellulose in ethanol. In *Nanotechnology for Bioenergy and Biofuel Production*, 2<sup>nd</sup> Edition. Springer: Cham, Switzerland; Berlin, Germany, pp. 153-171.
- [71] Risanto, L., Adi, D.T.N., Fajriutami, T., Teramura, H., Friasari, W., Hermiati, E., Kahar, P., Kondo, A., Ogino, C., (2023): Pretreatment with dilute maleic acid enhances the enzymatic digestibility of sugarcane bagasse and oil palm empty fruit bunch fiber. *Bioresource Technology*, 369: 128382.
- [72] Saha, B.C., Qureshi, N., Kennedy, G.J., Cotta, M.A., (2016): Biological pretreatment of corn stover with white-rot fungus for improved enzymatic hydrolysis. *International Biodeterioration and Biodegradation*, 109: 29-35.
- [73] Saravanakumar, T., Park, H.S., Mo, A.Y., Choi, M.S., Kim, D.H., Park, S.M., (2016): Detoxification of furanic and phenolic lignocellulosic derived inhibitors of yeast using laccase immobilized on bacterial cellulosic nanofibres. *Journal of Molecular Catalysis B Enzymatic*, 134: 196-205.
- [74] Selig, M.J., Viamajala, S., Decker, S.R., Tucker, M.P., Himmel, M.E., Vinzan, T.B., (2007): Deposition of lignin droplets produced during dilute acid pretreatment of maize stems retards enzymatic hydrolysis of cellulose. *Biotechnology progress*, 23: 1333-1339.
- [75] Singh, D., Chen, S., (2008): The white-rot fungus *Phanerochaete chrysosporium*: conditions for the production of lignin-degrading enzymes. *Applied Microbiology and Biotechnology*, 81: 399-417.
- [76] Singhvi, M.S., Kim, B.S., (2020): Current developments in lignocellulosic biomass conversion into biofuels using nanobiotechnology approach. *Energies*, 13: 5300.
- [77] Singhvi, M., Zinjarde, S., Kim, B.S., (2022): Sustainable strategies for the conversion of lignocellulosic materials into biohydrogen: Challenges and solutions toward carbon neutrality. *Energies*, 15: 8987.
- [78] Sudhakar, V., Naik, S.S., (2022): Hydrolysis a fermentation of lignocellulosic Biomass for Bioethanol. *Current World Environment*, 17(1): 113-121.
- [79] Tang, C.L., Shan, J.Q., Chen, Y.J., Zhong, L.X., Shen, T., Zhu, C.J., Ying, H.J., (2017): Organic amine catalytic organosolv pretreatment of corn stover for enzymatic saccharification and high-quality lignin. *Bioresources Technology*, 232: 222-228.
- [80] Tao, L., Aden, A., Elander, R.T., Pallapolu, V.R., Lee, Y.Y., Garlock, R.J., Balan, V., Dale, B.E., Kim, Y., Mosier, N.S., Ladisch, M.R., Falls, M., Holtzappple, M.T., Sierra, R., Shi, J., Ebrik, M.A., Redmond, T., Yang, B., Wyman, C.E., Hames, B., Thomas, S., Warner, R.E., (2011): Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using Switchgrass. *Bioresource Technology*, 102(24): 11105-11114.
- [81] Tayyab, M., Noman, A., Islam, W., Waheed, S., Arafat, Y., Ali, F., Zaynab, M., Lin, S., Zhang, H., Khan, D.I., (2017): Bioethanol production from Lignocellulosic Biomass by environment-friendly pretreatment methods: A Review. *Applied Ecology and Environmental Research*, 16(1): 225-249.
- [82] Tran, T.T.A, Le, T.K.P., Thanh, P.M., Nguyen, D.Q., (2019): Bioethanol production from lignocellulosic biomass. pp. 65-74. In Yun, Y. (ed.): *Alcohol fuels: current technologies and future prospects*, IntechOpen, London United Kingdom.
- [83] Trusi, A., (2019): A review on biomass: importance, chemistry, classification and conversion. *Biofuel Research Journal*, 22: 962-979.
- [84] Tu, W.C., Hallett, J.P., (2019): Recent advances in the pretreatment of lignocellulosic biomass. *Current opinion in green and Sustainable Chemistry*, 20: 11-17.
- [85] Umagiliyage, A.L., Choudhary, P., Liang, Y., Haddock, J., Watson, D.G., (2015): Laboratory scale optimization

- of alkali pretreatment for improving enzymatic hydrolysis of sweet sorghum bagasse. *Industrial Crops and Products*, 74: 977-986.
- [86] Vaidya, A.A., Murton, K.D., Smith, D.A., Dedual, G., (2022): A review on organosolv pretreatment of softwood with a focus on enzymatic hydrolysis of cellulose. *Biomass Conversion and Biorefinery*, 12(11): 5427-5442.
- [87] Valdez-Vazquez, I., Pérez-Rangel, M., Tapia, A., Buitrón, G., Molina, C., Hernández, G., Amaya-Delgado, L., (2015): Hydrogen and butanol production from native wheat straw by synthetic microbial consortia integrated by species of *Enterococcus* and *Clostridium*. *Fuel*, 159: 214-222.
- [88] Wang, W.H., Zhang, C.Y., Tong, S.S., Cui, Z.Y., Liu, P., (2018): Enhanced enzymatic hydrolysis and structural features of corn stover by NaOH and ozone combined pretreatment. *Molecules*, 23: 1300-1313.
- [89] Wang, W.T., Wu, B., Qin, H., Liu, P.T., Qin, Y., Duan, G.W., Hu, G.Q., He, M.X., (2019): Genome shuffling enhances stress tolerance of *Zymomonas mobilis* to two inhibitors. *Biotechnology Biofuels*, 12: 288-294.
- [90] Wi, S.G., Cho, E.J., Lee, D., Lee, S.J., Lee, Y.J., Bae, H., (2015): Lignocellulosic conversion for biofuel: a new pretreatment greatly improves downstream biocatalytic hydrolysis of various lignocellulosic materials. *Biotechnology Biofuels*, 8: 228.
- [91] Xu, N., Liu, S., Xin, F., Zhou, J., Jia, H., Xu, J., Jiang, M., Dong, W., (2019): Biomethane production from lignocellulose: biomass recalcitrance and its impacts on anaerobic digestion. *Frontiers in Bioengineering and Biotechnology*, 7: 191.
- [92] Yoo, J.-Y., Alavi, S., Vadlani, P., Amanor-Boadu, V., (2011). Thermo-mechanical extrusion pretreatment for conversion of soybean hulls to fermentable sugars. *Bioresources Technology*, 102: 7583-7590.
- [93] Yousuf, A., Pirozzi, D., Sannino, F., (2020): Fundamentals of lignocellulosic biomass. In *Lignocellulosic biomass to liquid biofuels*. Academic Press, pp. 1-15.
- [94] Zhang, Y., Wang, Z., Feng, J., Pan, H., (2020): Maximizing utilization of poplar wood by microwave-assisted pretreatment with methanol/dioxane binary solvent. *Bioresource Technology*, 300: 122657.
- [95] Zhang, J., Zhang, X., Yang, M., Singh, S., Cheng, G., (2021): Transforming lignocellulosic biomass into biofuels enabled by ionic liquid pretreatment. *Bioresource Technology*, 322: 124522.
- [96] Zheng, J., Rehmann, L., (2014): Extrusion pretreatment of lignocellulosic biomass: A Review. *International Journal of Molecular Sciences*, 15(10): 18967-18984.
- [97] Zhou, J., Cheng, H., Ma, J.F., Peng, M.G., Kong, Y., Komarneni, S., (2021): Persulfate activation by MnCuS nanocomposites for degradation of organic pollutants. *Separation and Purification Technology*, 26: 422-435.

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