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Review Article

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Insights into the recent advances in the pretreatment of biomass for sustainable bioenergy and bio-products synthesis: Challenges and future directions

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ABSTRACT

Recently, biomass has shown its viability as an alternative to fossil fuels. Due to the growing trend in greenhouse gas emissions generated by the continual burning of fossil fuel products, it will be advantageous for humanity to seek a more sustainable and renewable source of energy. Due to its availability, biomass has a promising approach as a feedstock for bioconversion processes that produce energy, fuels, and other chemicals. The carbon dioxide generated by burning biomass has no influence on atmospheric carbon dioxide since it is derived from a renewable source. Despite these benefits, its adoption in bioconversion and biorefinery processes has traditionally been hindered by its recalcitrant nature, as indicated by its intrinsic characteristics. Prior to any conversion process, biomass must be pretreated to enhance product recovery. To satisfy the rising need for renewable and sustainable energy sources, the present conversion efficiency must be improved and the biorefinery concept must transition from using just one biomass component (cellulose) to utilizing the complete biomass component. This study examines numerous pretreatment procedures used prior to any conversion process, the challenges faced, and the future of biomass pretreatment technologies. Physical, hydrothermal, chemical, oxidation, biological, and hybrid pretreatment techniques are evaluated. The review indicates that the ideal approach to biomass pretreatment must be able to deal with the recalcitrant nature of biomass, enhance the crystallinity of cellulose, and provide the greatest recovery of biofuels, bio-char, sugars, and other industrially relevant bioproducts. The data offered in this study will equip readers with the knowledge necessary to effectively identify solutions to pretreatment problems and energy generation from pretreated biomass.

Keywords: biomass pretreatment, biorefinery, bioconversion, sustainable energy, lignocellulosic biomass

INTRODUCTION

The global increase in energy demand has greatly contributed to greenhouse gas emissions with the industrial and transport sector as major contributors. Several countries have directly felt the impact of global warming on the environment and are committed to implementing the Paris Climate Agreement, which calls for the reduction of carbon emissions to tame the annual temperature increase to below 1.5°C. A lot of resources have been allocated to research to develop better technologies and policies that will quickly address the challenge of global warming. Alternative energy sources, which are environmentally friendly like solar, wind, hydropower, and biomass have been proposed (**Figure 1**).

Over time, the issue of the high cost of new technologies slowed down the transition to renewables. But in the last 10 years, the maturity in technological advancement has tremendously reduced the cost of renewables to even surpass hydropower (Ang et al., 2022). To effectively reduce carbon emissions in the environment, a robust alternative fuel is needed to replace fossil fuels. Since almost all sectors of human existence need a source of energy, an alternative compromise that is modern, less costly, and environmentally sustainable should be explored. On this basis, biomass has emerged as the most promising option with the lowest carbon emissions (Yang et al., 2022). Similarities between products gotten from biomass and that of fossil fuels make it the best substitute (Hlavata et al., 2014). Despite these advantages, one of the main causes of biomass under exploitation is the poor quality of biomass, which is often described in terms of its intrinsic characteristics (irregular size, energy density, bulk density, high moisture content, and low energy density) (Anukam & Berghel, 2020).

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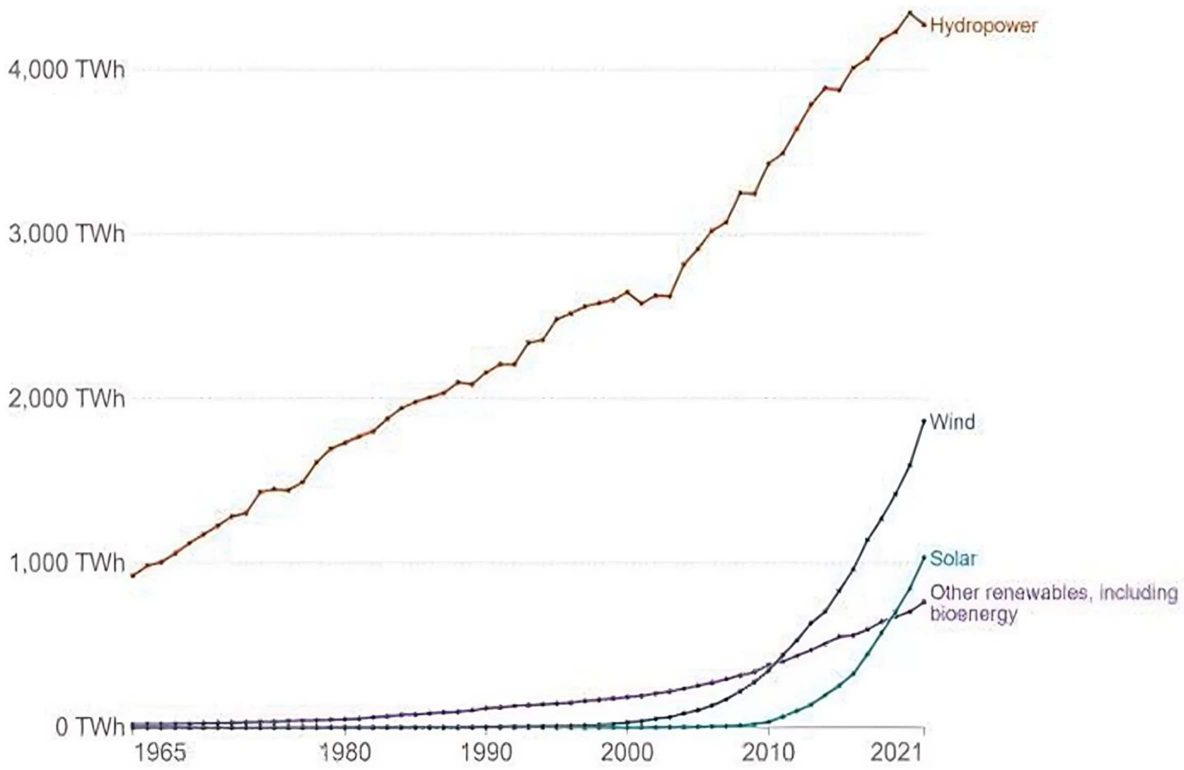

Figure 1. Modern renewable energy generation by source (Ritchie et al., 2022)

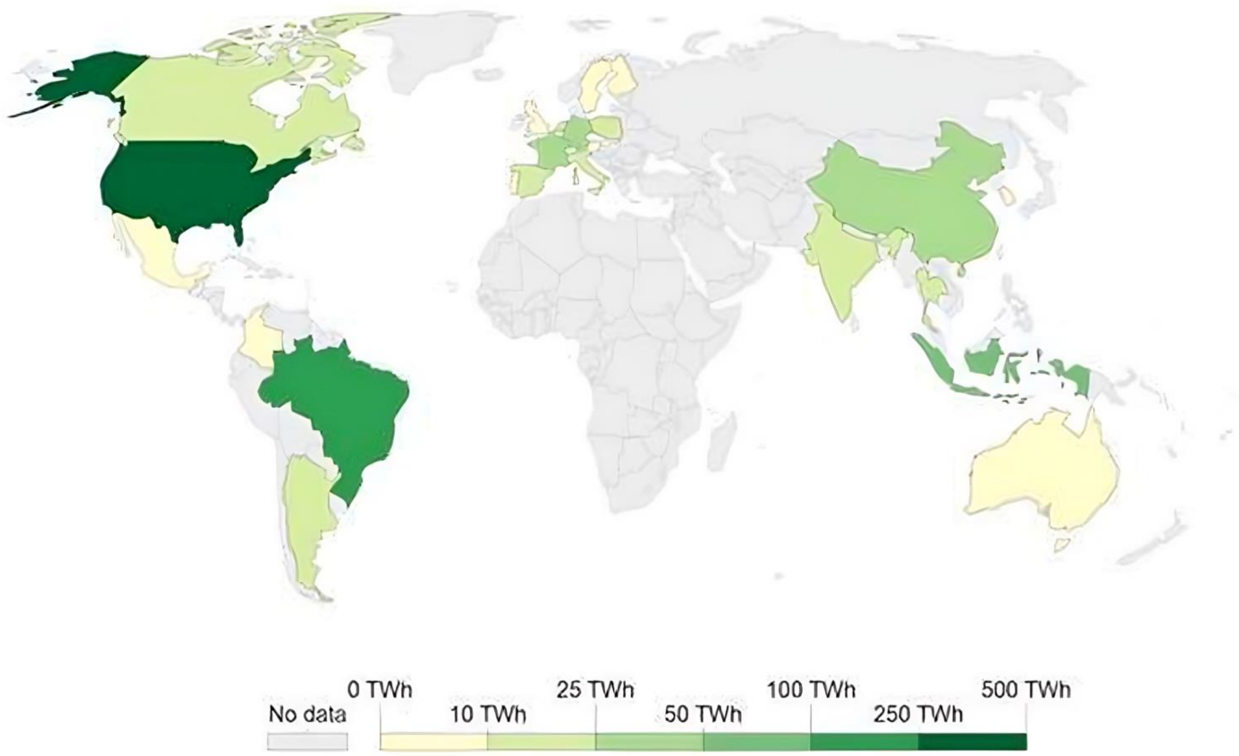

Figure 2. Biomass usage by region in the year 2021 measured in terawatts-hours (TWh) per year (Ritchie et al., 2022)

To maximize product recovery, biomass must be pretreated before any conversion process. The development of biochemical and thermochemical routes for the conversion of biomass to energy and other bio-products with minimal environmental implications has been the subject of intensive study. In contrast to the biochemical routes, which employ living organisms to convert biomass into gaseous and/or liquid fuels (e.g., bioethanol and biogas), the thermochemical route employs heat to disrupt the complex chemical structure of biomass (specifically, lignocellulosic biomass like wood) into a wide range of products, such as fuels, biochar, heat, chemicals, bio-oil, and power (Zhang & Zhang, 2019) (**Figure 2**).

The economic feasibility of the biomass energy generation process relies heavily on pretreatment, which results in structural, physical, and chemical changes to the biomass (Anukam et al., 2019). In this way, biorefinery and

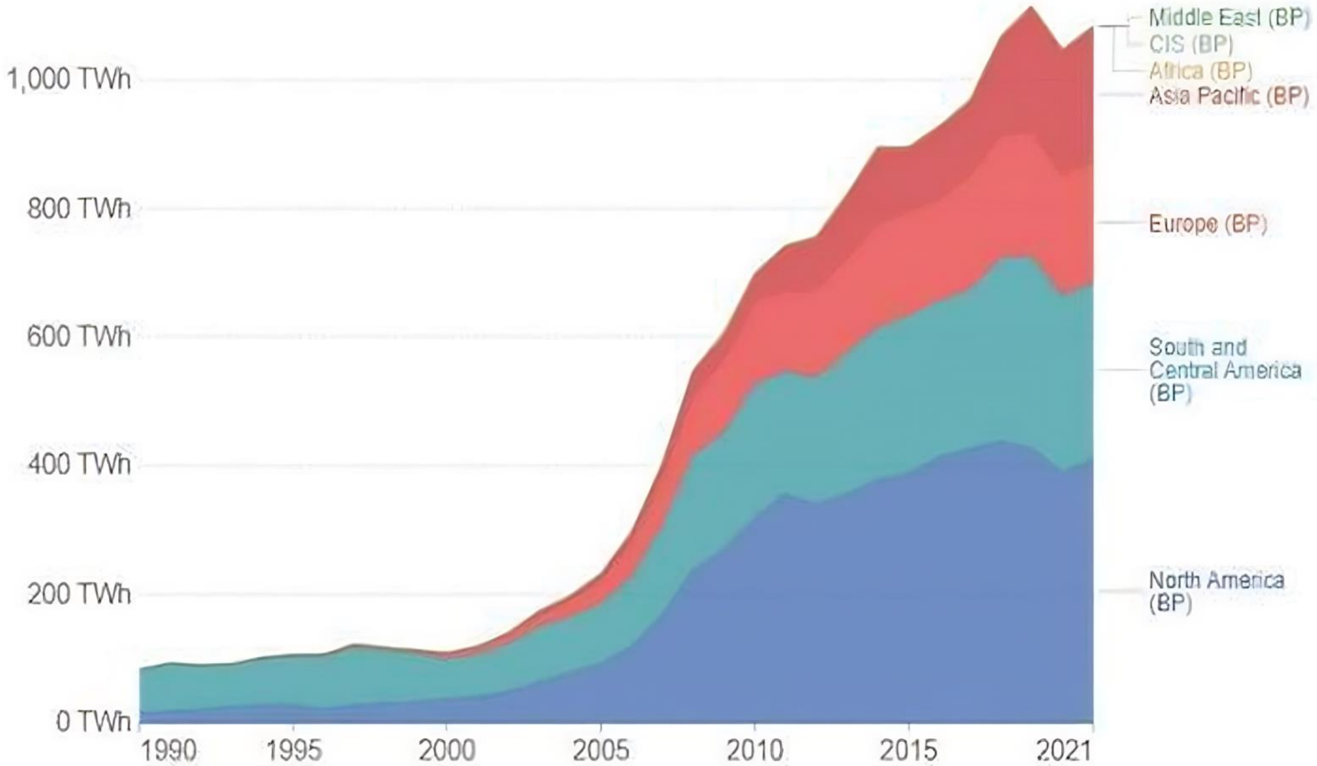

Figure 3. Biofuel production from biomass by region measured in terawatt-hours (Twh) per year (Ritchie et al., 2022)

bioconversion interests determine the pretreatment methods used for biomass (Lu et al., 2019). Biological, chemical, and physical pretreatments are only a few of the many types available. Later, we go into deeper depth on the various types of pretreatment.

The study of the processes involved in the conversion of biomass to energy and bioproducts is difficult because of the complexity of biomass itself. One of the biggest obstacles to researching the impact of altering biomass pretreatment and process parameters is the absence of high throughput, reliable and fast methods for analyzing and tracking biomass components important for energy generation and other value-added products (**Figure 3**).

Based on the scope of this study, the following are the primary research questions explored:

1. How does pretreatment improve lignocellulosic biomass quality to maximize product recovery? How does each method work? Which pretreatment method has better performance, and why do some thrive less?
2. How have pretreatment methods for bio-product synthesis processes evolved in recent years?
3. What are the main challenges that prevent the widespread use of today's improved biomass pretreatment methods?

In order to answer these research questions and better comprehend the properties of pretreated and non-pretreated biomass important to the production of fuels and chemicals, this review paper provides a critical assessment of Lignocellulosic materials and explores current methods of selective pretreatments, including extrusion, irradiation, steam explosion, deep eutectic solvents, wet oxidation, enzyme, and more, by researchers discussing the limitations of current pretreatment technologies. The rest of the article presents the advancements in bioenergy generation from pretreated biomass, the challenges of these technologies and suggestions to overcome them, and finally, the future of biomass pretreatment. It is expected that great progress will be made in the area of sustainable energy and chemical production from biomass as our understanding of the fundamentals of biomass pretreatment improves.

LIGNOCELLULOSIC MATERIALS

Lignocellulose-containing materials are typically composed of cellulose (40-50%), hemicellulose (25-35%), and lignin (15-20%). The variation of the amount of each component with the quality differs with the plant in question (Omiyale, 2022). Cellulose is a linkage of ß-1,4 glucosidic bound with glucose residues called 'cellobiose.' The structure of glucose exists in different levels of crystallinity index, which may be generally classified into crystalline (difficult digestion) and amorphous. Hemicellulose is a biopolymer of pentose (xylose and hexuronic acids), glucan, and hexose sugars (glucose, mannose, and rhamnose). Hemicellulose is degraded easily through dilute chemicals (Khan & Ahring, 2019).

Lignin, the primary recalcitrant moiety in a lignocellulosic material, is composed of aromatic constituents of carbon-to-carbon and carbon-to-oxygen chains such as p-coumaryl alcohol, synapyl alcohol, and coniferol alcohol unit (Yoo et al., 2020). However, its recalcitrant nature originates from the fact that it is covalently bonded to hemicellulose, making it an essential component of the lignocellulose complex. Biofuel and other bioproducts are challenging to synthesize without oxygen because it is hard to bond hemicellulose to lignin, crystallize cellulose, and degrade enzymes' access to the structure bonds. Therefore, the pretreatment and pre-

Table 1. Composition of some common sources of biomass (Sun & Cheng, 2002)

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Coastal bermudagrass	25	35.7	6.4
Corn cobs	45	35	15
Cotton seeds hairs	80-95	5-20	0
Grasses	25-40	35-50	10-30
Hardwoods steam	40-55	24-40	18-25
Leaves	15-20	80-85	0
Newspaper	40-55	25-40	18-30
Nut shells	25-30	25-30	30-40
Paper	85-99	0	0-15
Primary wastewater solids	8-15	NA	24-29
Softwoods stems	45-50	25-30	25-35
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Sorted refuse	60	20	20
Swine waste	6	28	NA
Switchgrass	45	31.4	12.0
Waste papers from chemical pulps	60-70	10-20	5-10
Wheat straw	30	50	15

processing of lignocellulosic materials are essential in achieving high yields of degradation products (Monlau et al., 2012, Olajuyigbe et al., 2019; Omiyale, 2022) (**Table 1**).

RECENT SELECTIVE PRETREATMENT OF LIGNOCELLULOSIC MATERIALS

Figure 4 shows the structure of lignocellulose material.

Physical Pretreatment

Physical pretreatment of biomass involves pre-processing methods that affect the pore space, grain size, crystallinity or amorphous cellulose, surface area, etc. It does not include adding chemicals or microorganisms (Jędrzejczyk et al., 2019). **Figure 5** shows the types of physical pretreatment.

Mechanical pretreatment

Mechanical pretreatment involves using various milling processes such as colloid, vibratory, hammer, grinding, mesh

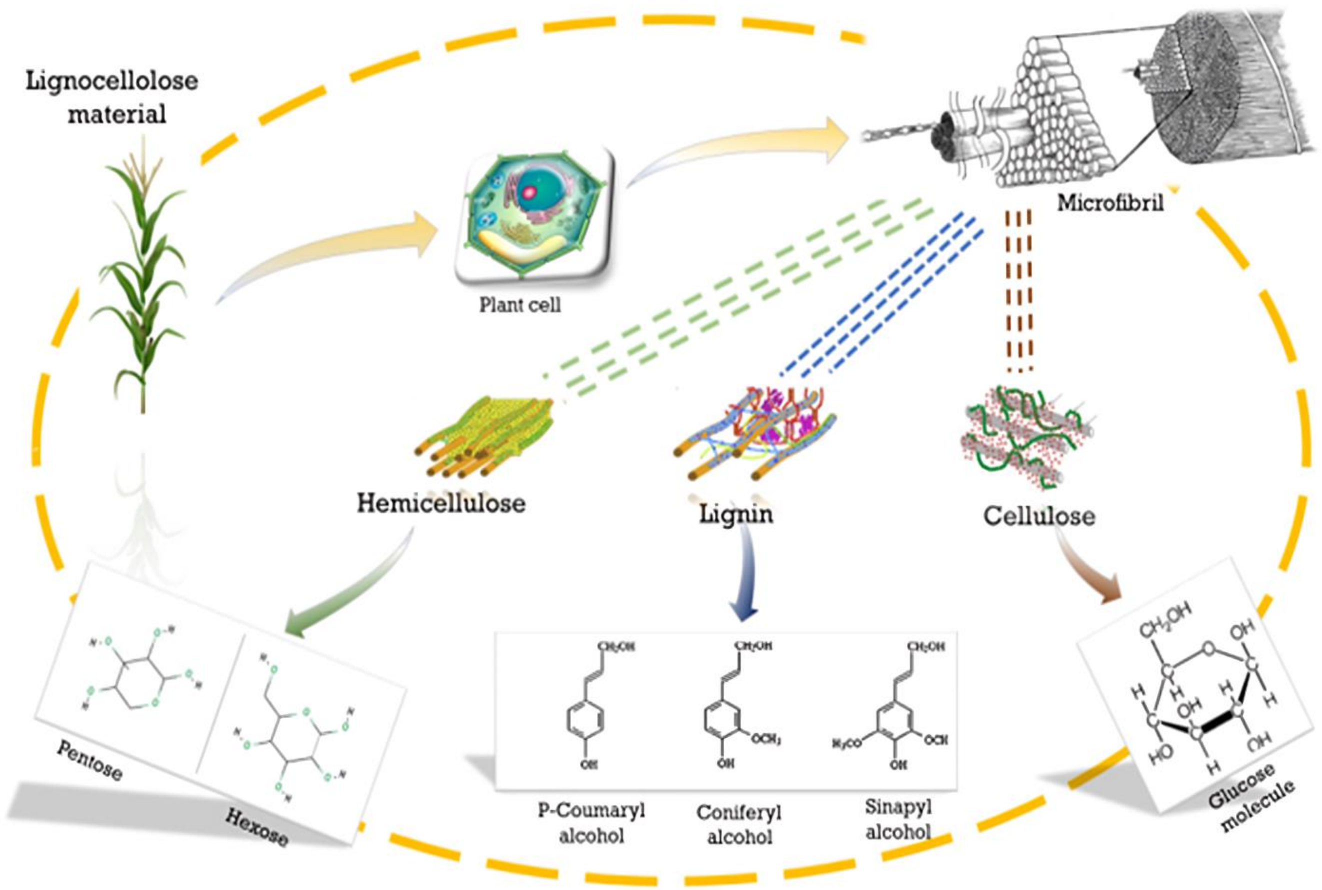

Figure 4. Structure of lignocellulose material (Khan et al., 2022)

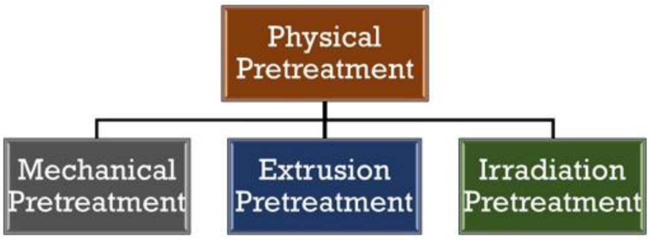

Figure 5. Types of physical pretreatment (Aftab et al., 2019)

grating, and sandpapering to organize the recalcitrant structure of lignocellulosic biomass. This type of pretreatment is supported by a biogas yielding experiment after mesh grating and sandpapering with 26% more yield over control (Tsapekos et al., 2016, 2018). In an investigation, degradation of rice straw by chip rolling was a more accessible particle size-dependent mainly due to a significant surface area increase and more hydrolysis enzyme exposure. Notably, particle size reduction far more than 0.35 mm to 1 mm can yield inhibition products such as fatty acids, eventually reducing the anaerobic digestion (Menardo et al., 2015).

Extrusion pretreatment

Extrusion pretreatment involves structure collapsing and shredding by forcing through a threaded die or tiny orifice. Heat is generated and forms a factor in the process. The effectiveness was proven in an experiment where rice straw was extruded and gave 40% more CH_4 yield than milled. (Tsapekos et al., 2015). Furthermore, adopting twin-screw extruders can further increase productivity by some 16.5% CH_4 yield. (Pérez-Rodríguez et al., 2018).

Irradiation pretreatment

Irradiation pretreatment typically involves high-energy beams with low wavelength (low energy) such as microwaves (10-1 m), which initiate a rapid spinning motion of molecules with opposing polarity leading to the increase in temperature and consequently enhancing its fractionation. In this case, into lignin and cellulose. Microwave pretreatment alone might not be sufficient enough to yield fruitful results with a wide margin. Still, success was recorded with microwave irradiation and ionic liquids at about 40-70% more cellulose saccharification (Ogura et al., 2014). Recent research has shown the use of a more powerful wavelength (10-8 m) like ultraviolet light, which has different effects based on the biomass type for irradiation pretreatment. A study using ultraviolet light on softwood and hardwood yielded a more significant result for softwood even though more pronounced effects were on pyrolytic than thermal stability, consequently leading to a reduction in lignin content and more oxygen content (Mattonai et al., 2021). Another study revealed that after corn straw was pretreated with ultrasonic waves (1.9 cm wavelength) a 6.86 ml/gd yield of CH_4 was produced over the untreated sample at 4.54 ml/gd CH_4 (Feng et al., 2013).

Hydrothermal Pretreatment

Figure 6 depicts the types of hydrothermal pretreatment.

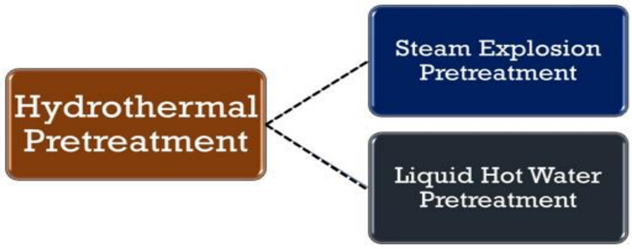

Figure 6. Types of hydrothermal pretreatment (Sarker et al., 2021)

Liquid hot water pretreatment

This hydrothermal pretreatment involves boiling water (maintained in liquid form) at an elevated temperature of about 160-200 °C and increasing the vapor pressure to 0.3 psi to generate smaller subunits of hemicellulose, de-lignification, and increased biomass surface area (Ren et al., 2020). Researchers became very popular with the liquid hot water pretreatment method due to the cost advantage over older, costlier chemical methods (Ji et al., 2020). At the end of various studies, LHWP significantly increased the yield of bioproducts by about 3% more when combined with other methods (Wang et al., 2016, 2021).

Steam explosion pretreatment

Boiling water is maintained as saturated steam (160-250 °C) in a pressured container (72.5-725.2 psi) for a short time then pressure is dropped suddenly to disrupt the recalcitrant nature of the biomass (Zheng et al., 2014). Hemicellulose usually gets broken down with the additional significant transformation of lignin and conversion of acetyl branches of hemicellulose to organic acids, which also catalyzes the reaction in a favorable direction and contributes to easier digestion of the lignocellulosic biomass (Lee et al., 2020). This method is generally referred to as a cost-effective and greener pretreatment compared to chemical methods, as no toxic waste is produced from chemicals or catalysts (Khan et al., 2022).

Chemical Pretreatment

Employing chemical solutions in de-lignification, easy anaerobic digestion, and bioproducts/biofuel yield from biomass has perks and drawbacks, as do all pretreatment methods. Chemical methods gained the most concern about the ecotoxicity of wastes and chemical persistence in the environment (Khan et al., 2022). Some perks include efficient liquidation of bound components, pore size, and increase in surface area, but concerns are still on converting degraded sugars to furfural. A study on acidic pretreatment led to dehydration of hemicellulose to hydroxymethylfurfural and furfural and again to unwanted solids, which accounted as false lignin when being analyzed (Amiri et al., 2014; He et al., 2020; Zhao et al., 2012). However, there is the problem of adherence of this fake lignin onto cellulose surface to hinder efficient anaerobic digestion. Due to recent outcry in support of green earth, the friendliest chemical types now furnish biodegradability and reduced toxicity (Khan et al., 2022). **Figure 7** depicts recent chemical pretreatments.

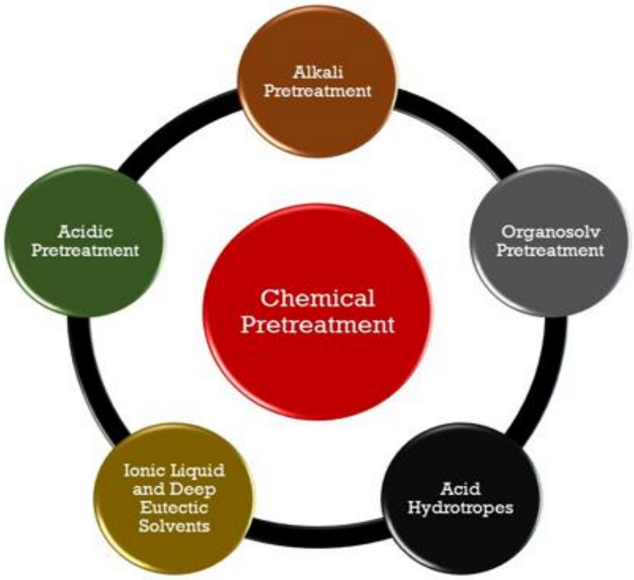

Figure 7. Types of chemical pretreatment (Aftab et al., 2019)

Alkali pretreatment

Alkali pretreatment forms one of the traditional methods researchers use because of its action on biomass surface area, pore size improvement, and breakdown of hemicellulose into sugar (Usman et al., 2014). Alkali breaks the ester linkages of lignin, cellulose, and hemicellulose, leading to amorphous in cellulose, dissolution of lignin, and ultimately improved downstream processes (Usman et al., 2014). Some of the most widely used alkali in this method, according to Usman et al. (2014), are calcium oxide, potassium oxide, ammonia, and urea (Siddhu et al., 2016). According to Khan et al. (2022), an improved CH4 yield of 56.4% was recorded using potassium oxide for pretreatment over non-pretreated corn stover. In the case of ammonia, it stabilizes the pH conditions and also adds to the bioproduct yield by 9% (Khan et al., 2022).

Acidic pretreatment

The biomass undergoes pretreatment using organic and inorganic acids such as HNO3, H3PO4, C4H4O4, H2SO4, and HCl (Ilanidis et al., 2021). It is a standard procedure to carry out pretreatment involving concentrated acids containing 30-70% at temperatures under 100 °C and those using dilute acids at around 100-250 °C. The acids can be recovered for continuous use (Zheng et al., 2014). A study on the pretreatment of wheat straw recorded an increased bioproduct yield of 15% for 60 minutes.

Organosolv pretreatment

Orgnolv pretreatment involves the use of organic solvent for pretreatment. This chemical pretreatment is done with solvents characterized by low boiling points (ethanol and acetone). It can be catalyzed or not with excellent results. However, sulfuric/oxalic acid (acid/base) as catalysts yielded better de-lignification (Huijgen et al., 2011; Yao et al., 2018). This proved very effective on all types of biomasses but with serious lignin modification due to burning from high temperatures (Meng et al., 2020a).

An example is CELF (Co-solvent enhanced lignocellulosic fractionation). A pretreatment method employs THF (tetrahydrofuran), a neutrally charged and chemically inert solvent, and water as a solvent mixture. Studies have proved it is very effective in lignin removal (by hydrophobic interaction) and the breakdown of polysaccharides (Mostofian et al., 2016; Smith et al., 2016). An example is the corn stover experiment where Co-solvent enhanced lignocellulosic fractionation yielded 95% pentoses and hexoses over pretreatment by dilute acids (Nguyen et al., 2015).

GVL (gamma-valerolactone) is another example of a co-solvent for lignocellulosic pretreatment. It is produced from sugar disruption, HMF, and levulinic acid products (Ding et al., 2014; Mostofian et al., 2016). It is inert, mixes in water, and possesses a low melting temperature (Raj et al., 2021). It is also reportedly eco-friendly and biodegradable and has applications in manufacturing polymers and bioproducts (Kerkel et al., 2021). Its mechanism of improving sugar yield is due to breaking 1-4 glycosidic bonds (Luterbacher et al., 2014).

Acid hydrotropes

Acid hydrotropes are recent biomass pretreating solvents such as benzene sulfonic, maleic acid, etc. (Cai et al., 2020). Its de-lignification properties are due to its amphipathic nature. The water-hating lignin is shielded away from the lipophilic areas of the solvent through pi-pi interaction, which is then separated by dilution with water below its aggregate temperature (Ji & Lv, 2020).

The acid hydrotrope eliminated the challenge of high reaction time and temperatures (about 150 °C) caused by aromatic salt-containing hydrotropes, which are primarily used in the pulp-making industry. This advancement improved pretreatment by reducing the reaction time and temperatures to below 30°C (Zhu et al., 2019).

Ionic liquids and deep eutectic solvents

Another recent pretreatment solvent is the ionic liquids. They are salts of organic origin that possess melting points below 100 °C. They are also widely reported as non-toxic and eco-friendly. This is due to their high thermal stability and low vapor pressure making a recovery and re-use possible. (Mallakpour & Dinari, 2012). Diakylimidazolium, chlorine, and protic ionic liquids have recently gained more popularity among green chemistry researchers (Zhang et al., 2021). The organized nature of the lignocellulosic biomass is disrupted by competition for hydrogen-bonded compounds (Agbor et al., 2011).

Deep eutectic solvents (DES) possess almost similar properties as Ionic liquids. However, ionic liquids are cationic and anionic. At the same time, deep eutectic solvents contain two or more solids bonded together in hydrogen bonding to form a compound with a much more reduced melting point of the separate solids (Smith et al., 2014). They can be formulated from cheap derivatives. An example is chlorine chloride, which is cheap, eco-friendly, and, most importantly, can receive hydrogen bonds.

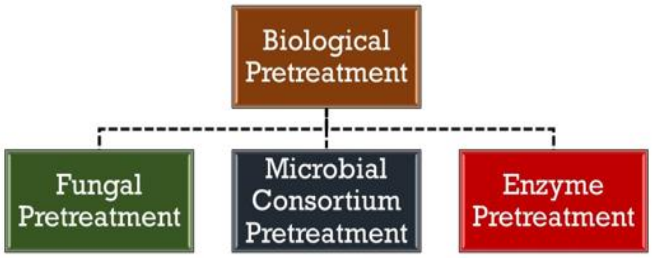

Figure 8. Types of biological pretreatment (Aftab et al., 2019)

Oxidative Pretreatment

Oxidative pretreatment includes the types, as shown in **Figure 8**.

Wet oxidation pretreatment

The biomass is wet with water and oxidized through oxygen-donating species such as hydrogen peroxide, air, oxygen, and ozone. The system's temperature and pressure increase to 130-350 °C and 5.5-2,900.8 psi, respectively. The oxygen-donating species generate free radicals, which increases the reaction rates by bombarding the lignocellulosic biomass (Khan et al., 2022). The wet oxidation pretreatment was used in a study by (Almomani et al., 2019; Hendriks & Zeeman, 2009), but it caused a loss of hemicellulose and lignin matter.

Advanced wet explosion pretreatment

This type of oxidative pretreatment is an improvement in wet explosion pretreatment. How successful the method will be, depends significantly on factors such as temperature, pressure, and time of the process. The system's temperature is around 140-220 °C and pressure about 75.5-2,900.8 psi. Then there is provision for a sudden drop in pressure in the bioreactor. This method was initially studied by (Ahring et al., 2015; Biswas et al., 2014).

The process effectively breaks down hemicellulose into sugars, facilitates the de-esterification of hemicellulose acetyl groups to produce organic acids, and carries out de-lignification into hemicellulose and cellulose. (Ahring et al., 2015, Georgieva et al., 2007).

Biological Pretreatment

This method employs the use of enzymes or enzyme-producing microbes. Enzymes including cellulases (endoglucanase, exoglucanase, and β-glucosidase) and hemicellulases are used to break down the organized cellobiose β-1,4 glycosidic linkage at various points to generate high yield D-glucose (Khan et al., 2022; Omiyale, 2022). The enzyme-producing microorganisms can be actinomycetes, fungi, and bacteria (Olajuyigbe et al., 2019). The biological method is considered eco-friendly but might be pricey (Usman et al., 2020). Biological pretreatment includes the ones, as shown in **Figure 9**.

Fungal pretreatment

Fungal pretreatment involves using fungi found naturally in decaying wood. These fungi are used to attack the lignin or cellulose component. They are generally classified into brown, soft, and white rot fungi due to their activity in different conditions of temperature and pH, as they are found naturally in different niches (Wagner et al., 2018). A study (Shah et al., 2019) reported that fungal Pretreatment (bacillus species) on rice straw generated 76% more biofuel than untreated and generally exhibited low lignin content.

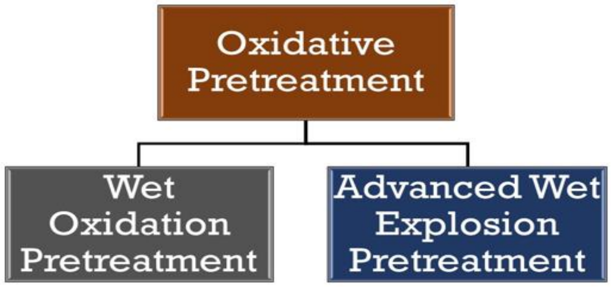

Figure 9. Types of oxidative pretreatment (Zhou et al., 2022)

Microbial consortium pretreatment

This type of biological pretreatment involves using enzyme-producing microorganisms that can co-exist naturally or by adaptation in pretreatment activities (Omiyale, 2022). The enzymes produced are purified and used for pretreatment, or the microbe growth is allowed to yield the enzyme directly into the medium (Olajuyigbe et al., 2019). Omiyale (2022) reported a 2% D-glucose yield from the fungal consortium of cyberlindnera fabianii and pichia kudriavzevii over untreated corn cob biomass.

Enzyme pretreatment

Enzyme pretreatment involves the introduction of cellulose, hemicellulose, and laccase (lignin breaking) produced by enzyme-producing microbes. This method is considered the slowest. Substantial reduction in sugar yield, as evident in the direct introduction of microbes, is absent in this method (Khan et al., 2022). The major drawback is the high cost of enzymes, which sometimes may not be commensurate with the yield of bioproducts. Processes that require anaerobic digestion of biomass to yield CH4 do not commonly practice this pretreatment because of the low yield mentioned (Shi et al., 2021; Zheng et al., 2014) (**Table 2**).

Hybrid Pretreatment

Some promising pretreatment methods are combined to minimize individual disadvantages (e.g., cost and incomplete process) by taking advantage of their synergistic properties (greater efficiency). Researchers have experimented over time and have reported successes (Usman et al., 2019a).

The combination of thermal and chemical methods studied by (Dutta et al., 2022) eliminated the problems of very low pH and the production of toxic derivatives, which interfere with bioproducts (Usman et al., 2019b). Another combination that works synergistically is physical and biological pretreatment. A study revealed that the pretreatment of biomass with fungi and chemical/physical pretreatment makes a cheap and eco-friendly approach to producing D-glucose and fuel (Shirkavand et al., 2016).

Some other combinations that work for some reason are shown in **Table 3**.

Table 2. Pretreatment enzymes and functions

Enzyme system	Scientific name	Function	Reference
(Cellulase) endoglucanases	Endo-1,4-β-D-glucan 4-glucanohydrolase	Hydrolyses, at random, α-1,4 glucosidic bonds at internal amorphous sites	Omiyale (2022)
(Cellulase) cellobiohydrolases	1,4-β-D-glucan cellobiodehydrolase	Act on the reducing or nonreducing ends of cellulose chains, liberating cellobiose	Omiyale (2022)
(Cellulase) β-glucosidases	β-glucoside glycosyl hydrolase	Hydrolyze cellobiose or cello-oligosaccharides to glucose	Omiyale (2022)
Laccase	Glycoprotein	Breaks down lignin	Khan et al. (2022)

Table 3. Hybrid pretreatment

S/N	Methods in combination	Biomass	Synergistic advantage	Reference
1	Ultrasonic vs. electrolysis	Mix microalgae biomass	Low energy inputs, low costs	Kumar et al. (2017)
2	Wet-oxidation vs. alkali	Sewage sludge	Reduced inhibitors generation	Khan and Ahring (2019)
3	Wet-oxidation vs. steam explosion	Sewage sludge	Overcomes large particle size & hard biomass	Khan and Ahring (2021)
4	Ionic liquids vs. ultrasound vs. microwave	Eucalyptus saw dust	More cellulose saccharification, more de-lignification, hemicellulose digestion, erosion of crystalline parts	Beig et al. (2021) & Ogura et al. (2014)
5	Thermal vs. chemical	Wheat straw	More biomass solubility	Dutta et al. (2022) & Usman et al. (2019a)

A literature search on PubMed on pretreatment hybrid studies compared with single pretreatment works yielded significantly more results in favor of single studies. More hybrid studies need to be done to discover more sustainable synergistic benefits.

CHALLENGES AND FUTURE OF BIOMASS PRETREATMENT

It has been established that pretreatment is essential and significantly determines the quality of biofuel, sugars, and other downstream products that will be generated. The ultimate aim of pretreatment is to modify/bypass inherent structural barriers to biomass hydrolysis for the specific end product (lignin alcohols, sugars, biofuels, etc.). Therefore, the specific end products dictate the pretreatment methods to be used. Some problems encountered during biomass pretreatment can be worked on to improve the processes for better practices (**Table 4**).

The mechanical reduction of biomass size increases the accessibility of pretreatment solvents or microorganisms, which favors bio-product production. Still, excessive size reduction must also be accounted for, as this poses a challenge at more than 0.35 mm to 1 mm. The broth produces inhibition products such as fatty acids due to the bioreactor contents' reduced surface thickness of the broth layer. This disrupts the anaerobic degradation process after pretreatment (Menardo et al., 2015). Heat generation may also play a role in excessive

Table 4. Summary of challenges and future of biomass pretreatment

Pretreatment	Challenges	Recent advances	Reference
Solvents	Residual contamination by sugars, requires greater than 50% acid hydrotopes solvent therefore these is fear of acidity problem.	Recyclability/reuse of solvents and catalysts, low energy requirements for recycle, low cost bioproduction of solvents, low toxicity and eco-friendly, specifically designed to overcome shortcomings of traditional methods relating to harshness (structural degradation of product of interest), reactor design to counter solvent acidity, compatibility of solvents with multiple feedstocks for increased yield & rating of cellulose, lignin, & hemicellulose (some ionic liquids and DES), use of AI for solvent performance & behavior predictions.	Hennequin et al. (2021) & Kim and Yoo (2021)
Physical	Greatly reduced particle size of biomass minimizes the thickness of broth layer in the bioreactor (e.g., halts CH_4 outflow), high energy requirement, does not remove lignin.	Even though it is quite straightforward, eco-friendly as no toxic waste is generated or for anaerobic digestion inhibition. It consumes energy & is therefore costly (e.g., irradiation is mostly used for experiment purposes as its expensive on a commercial scale).	Sankaran et al. (2020), Bochmann and Montgomery (2013), & Chaturvedi and Verma (2013)
Hydrothermal	High energy requirements, little significant yield improvement, higher temperature resulted in furfural & formic acid unwanted products.		Alvira et al. (2010) & Ji et al. (2022)
Chemical	High alkaline concentration (NaOH) was still toxic for microbes after washing, very difficult to reuse. Acid causes degradation of sugars to furfural, HMF, fake lignin that inhibits hydrolysis.	Research suggests alternative use of KOH as its beneficial for reactor microbes instead.	Shinde et al. (2018)

Table 4 (continued). Summary of challenges and future of biomass pretreatment

Pretreatment	Challenges	Recent advances	Reference
Biological	Unfinished removal of lignin from its bound state leading to formation of unwanted microbe-inhibitory intermediates during downstream processes though relatively green economy friendly, needs more time in the reactor than other methods, microbes deplete sugars.	Slow hydrolysis rate determining process is being improved with enzymes of high hydrolytic activity, subject biomass to very short fungal pretreatment as extensive pretreatment may deplete sugars for improved bioproducts/biofuel yield.	Taherzadeh and Karimi (2008) & Shirkavand et al. (2016)

power consumption characteristic of the physical pretreatment methods.

The chemical pretreated biomasses generate fake lignin, composed of HMF and furfural, which adhere to the cellulose surface, disrupting anaerobic digestion efficiency. Recovery of pretreatment chemicals is difficult under chemical pretreatment. NaOH, an example of alkali used to pretreat biomass, is toxic to microbes even after washing due to the concentration needed for effective pretreatment (He et al., 2020).

A challenge mostly related to biological pretreatment is the cost of enzymes needed. This is because such enzymes come as highly purified products. Isolation of microorganisms and stimulating them to produce lignocellulosic enzymes may be a better option (Omiyale, 2022). Even with the successes of this method, it is still considered the slowest kind of pretreatment and then the problem of microbes depleting sugars produced in the bioreactor remains another challenge (Khan & Ahring, 2021). This results in the availability of little sugars for conversion to bioproducts/biofuels.

The use of organo co-solvents in biomass pretreatment is showing new possibilities. They show effective pretreatment on woody and herbaceous biomass (Meng et al., 2020a). Gamma valerolactone, a solvent used in the production of bio-pharmaceuticals and polymers, exhibits many advantages, such as being eco-friendly, chemically stable, miscible with water, possessing low melting temperature, and showing better pretreatment results under the same mild conditions with other co-solvents. However, its boiling point of approximately 207 °C makes its recovery extremely difficult (Galbe & Wallbwerg, 2019).

Acid hydrotropes cause unwanted residual sugar contamination, amongst other drawbacks of their use, such as water, solvent, and energy consumption. Future reactors are recommended to be built with the particular acidity potentials of the reaction mixture of this solvent in mind, as high concentrations of the solvents are needed. Ionic liquids are characteristic of energy-intensive recovery processes and non-sustainable as they are produced from petroleum, which raises concerns about price and eco-toxicity. Before most of the newer solvents can be made commercially available, these technical problems mentioned need to be adequately addressed (Kim & Yoo, 2021).

FUTURE OF BIOMASS SOLVENTS

The old methods used for pretreatment solvent include de-lignification, high sugar release, and re-use of solvents. These methods brought about the use of sugar-centric methods, which involve the use of catalysts and widely accepted new solvents, which have been reported to be eco-toxic, yield badly disrupted lignin due to harsh reactions. Future solvents should be made to meet these conditions, such as the recovery of high-quality lignin (not just de-lignification), derivation from sustainable sources, and non-toxicity.

DES' recovery and product quality upgrade are difficult because of the tough hydrogen bond between the solvent and the fractionated biomass. More research on how to further advance processes such as anti-solvent use, solid-liquid extraction, and liquid-liquid extraction should be worked on. Special care should be taken to eliminate intermediates from the pretreatment process in the DES used before re-use (Isci & Kaltschmitt, 2021). Ionic liquids and DES do not require the addition of acids or base catalysts as some solvents require because they will further aid the prevention of intermediate inhibitors. As a recent advancement, research into ionic liquids and DES that preserve lignin quality is ongoing, as documented by (Chen et al., 2020; Dutta et al., 2017). The future focus should be on research into less energy-intensive ionic liquids solvent recovery processes and re-address production sources, as petroleum production is expensive and not sustainable.

Studies revealed that γ-VL as a pretreatment solvent outperformed other solvents under less harsh methods. However, difficulty arises during solvent removal for re-use because it possesses a boiling point of 207 ^{o}C, which makes the process tedious. In recent advances to this method, precipitation, then distillation in combination with liquid carbon dioxide, is used for recovery, which has been largely successful (Galbe & Wallberg, 2019).

Lignin-Centric Valorization

Employment of methods, solvents, etc., which create unwanted lignin structure condensation during pretreatment and create problems during downstream processes should be avoided. A study researched the use of formaldehyde in protecting the ether bonds of lignin through forming acetal links with alpha and gamma OH-groups of lignin side groups. Dong et al. (2019), Liu et al. (2021), Meng et al. (2020b), and Shuai et al. (2016) used 1,4-butanediol and cyrene to protect the lignin, and their results follow a pattern of preserved lignin linkage. As a new addition, a catalyst should be introduced to break down lignin immediately after it is freed to produce aromatic subunits and carbohydrates (Luo et al., 2021).

Considering Hemicellulose

Hemicellulose constitutes approximately 35% of lignocellulosic biomass. However, the attention of many researchers is mostly on lignin and cellulose but not on hemicellulose, even with its apparent components used with cellulose in fermentation and other biological processes, conversion to oil, etc. Due to the tedious separation process, most processes precipitate out lignin and discard hemicellulose with catalysts and water. More research and focus should be targeted on the use of hemicellulose (Kim & Yoo, 2021).

Accounting for Solvents in Process Design

The use of design software to simulate bioreaction should account for solvents to generate fast data and give an in-depth analysis of the entire process. (Seidl & Goulart, 2020).

CONCLUSIONS AND RECOMMENDATIONS

The fundamental objective of meeting community needs linked to energy and environmental security is to develop secure and resilient systems for the sustainable conversion of biomass.

There is a need for enhanced pretreatment, saccharification, and fermentation technologies that would allow for more affordable and ecologically friendly conversions. Cellulose has been developed as a biomaterial for biofuels such as biocrude and platform chemicals for creating additional biomaterials with added value. This is anticipated to contribute to the development of a practical, cost-effective, and environmentally friendly method of producing these materials. Anaerobic digestion of lignocellulosic materials that had been processed to lessen the complexity of lignocellulose's structure resulted in a greater quantity of methane; this research examines the different pretreatment techniques used. Physical, hydrothermal, chemical, oxidation, biological, and hybrid pretreatment techniques are evaluated. The following conclusions may be taken from this review:

1. Extreme physical pretreatments are unneeded and may be rather costly owing to their high energy requirements.
2. The assessment indicates that the ideal approach must be able to handle the recalcitrant character of biomass, enhance the crystallinity of Cellulose, and provide the greatest recovery of biofuels, bio-char, sugars, and other industrially important bioproducts.
3. Alkali pretreatments, in particular, are beneficial for anaerobic digestion; nonetheless, they might cause secondary environmental issues.
4. Although breakthroughs have been achieved in physical and chemical pretreatments, their commercialization has been difficult due to increased energy consumption and sophisticated procedures.
5. It has been shown that biological pretreatments are necessary for the anaerobic digestion of lignocellulosic materials and are more environmentally friendly than chemical pretreatments.

However, the presence of inhibitory compounds produced during pretreatment remains a barrier to the efficient and complete use of lignocellulosic material during anaerobic digestion. Therefore, it is vital to develop low-cost, high-efficiency, and environmentally friendly pretreatment techniques for lignocellulose material to assure its optimal usage in anaerobic digestion, while simultaneously addressing the barriers to the general adoption of these pretreatment methods.

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