



Assessment of Pretreatment Strategies for Valorization of Lignocellulosic Biomass: Path Forwarding Towards Lignocellulosic Biorefinery

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Abstract

The continuous depletion of fossil resources, energy-crisis, and environmental pollution has become the main drivers for the transition of linear petroleum-refinery to a sustainable biorefinery. Lignocellulosic biomass (LCB) remains the most abundant underutilized renewable biomaterial on our earth that offers a sustainable production of various value-added products like biofuels and other platform chemicals. However, presence of impenetrable lignin sheath along with highly crystalline structure of holocellulose barricades its commercial utilization. In this context, a suitable pretreatment method is mandatory to reduce the recalcitrance of the LCB material. Pretreatment capabilities derived from the extraordinary conditions for its effectiveness in laboratories and even at industrial scale for conversion of LCB are limited. In order to make these LCB bioconversion processes economically viable, more research is needed to focus on developing biorefinery approach. In current scenario, a pretreatment method that can fractionate the variety of LCB to produce lignin free carbohydrates with negligible waste biomass generation is of utmost need. Therefore, to promote the emerging technologies, the present review summarizes the recent advances in the most advanced pretreatment technologies being utilized for the LCB based biorefinery. Pros and cons associated with various pretreatment methods have been critically reviewed. Further, efforts have been made to create a better understanding of the already researched pretreatment technologies to facilitate the future research direction to realize the idea of biorefinery an actuality.

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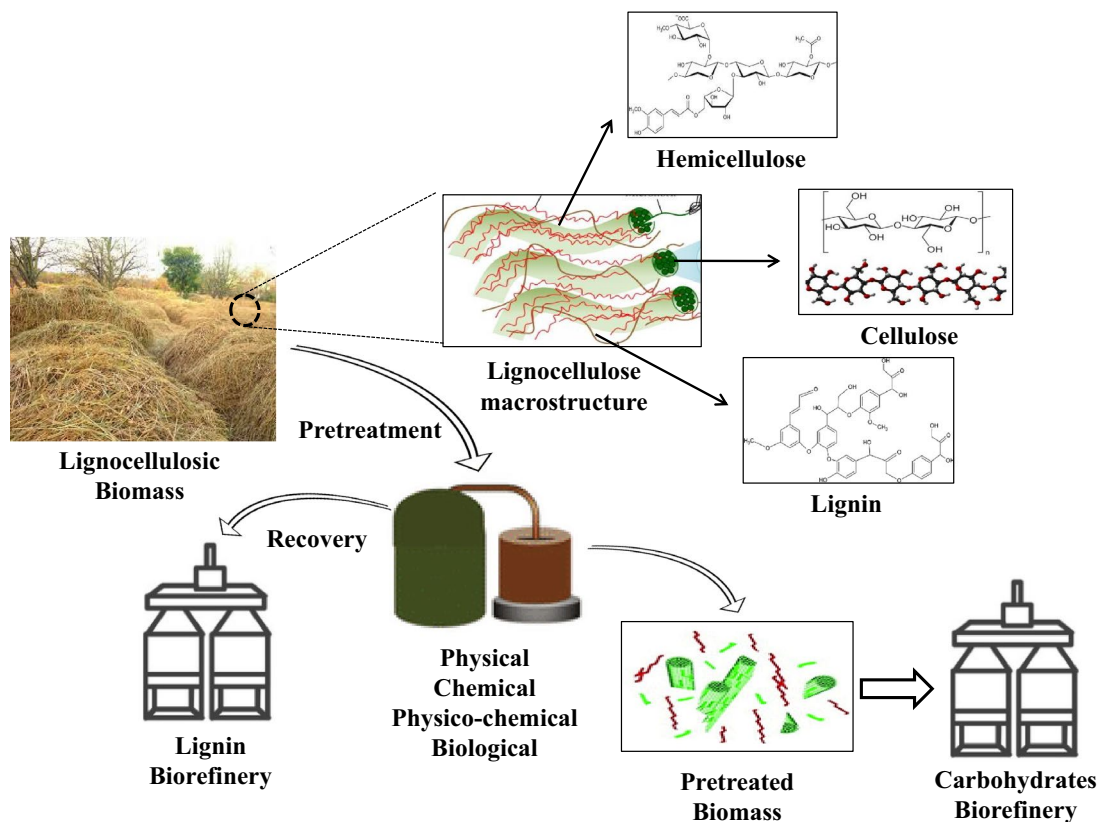
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Graphical Abstract

*Highlights*

- Pretreatment methods for valorization of LCB have been extensively reviewed
- Applicability of pretreatment methods to LCB biorefinery has been discussed
- Mechanisms of pretreatment methods have been discussed
- Challenges associated with pretreatment methods have been highlighted

Keywords Pretreatment · Lignocellulosic biomass · Biorefinery · Biomass valorization · Biofuels

Abbreviations

AFEX	Ammonia Fiber Explosion
COD	Chemical oxygen demand
CRI	Cellulose crystallinity index
CSF	Combined severity factor
DES	Deep Eutectic Solvent
GVL	g-valerolactone
HMF	5-hydroxymethyl furfuraldehydes
IL	Ionic liquid
MW	Microwave
MWAP	Microwave Assisted Pretreatment

NADES	Natural Deep Eutectic Solvent
LCB	Lignocellulosic biomass
PEF	Pulsed Electric Field
S/L	Solid/Liquid
Sc-CO ₂	Supercritical Carbon Dioxide
SDS	Sodium dodecyl sulfate
Temp	Temperature
TRS	Total reducing sugars
TS	Total solids
US	Ultrasound
US DOE	US Department of Energy

Statement of Novelty

The novelty of this review lies in its comprehensive analysis of recent advances in pretreatment technologies especially for lignocellulosic biomass, with a focus on fractionating the biomass to produce lignin-free carbohydrates while minimizing waste biomass generation. By critically evaluating the pros and cons of various pretreatment methods, this review not only consolidates existing knowledge but also provides insights into the future research directions required to realize the concept of a LCB-based biorefinery. This comprehensive review serves as a valuable resource for researchers and industry professionals aiming to overcome the barriers associated with LCB utilization and facilitate the transition towards a sustainable and economically viable biorefinery approach.

Introduction

Energy is placed in the core of the most crucial sectors for development of human race. It acts as an essential factor for determining the socio-economic and high living standards of a country. Drastic increase in global human population and industrialization has exponentially increased the energy demand. Currently, fossil-based energy sources such as oil, coal, and natural gas are the major non-renewable resources are being used to accomplish the increasing energy demands. Concern over the exhausting fossil fuel resources and environmental pollution has extremely influenced the global scientific interest towards biofuels and other renewable energy sources. The transition from linear petroleum refinery to renewable biorefinery process is identified as a crucial step towards the progress of a viable industrialization, energy independence, and efficient management of greenhouse gas emissions. The US Department of Energy (US DOE) has identified 15 ideal target chemicals including biofuels and value-added bio-chemicals, as a result of conversion of biomass through a biorefinery platform [1]. Different types of biological materials such as agricultural residues, forest residues, and municipal solid waste; generally referred as lignocellulosic biomass (LCB) are being produced globally in massive capacities and remained underutilized. These biomasses are composed of several types of chemical entities, which may act as starting points for the production of large variety of value-added products, platform chemicals, or intermediates through different biochemical/chemical conversion routes. The value addition to the hugely abundant, cheaper,

and renewable carbon source in the form of biomass may deliver substantial benefits in response to reducing fossil fuel resources and increasing environmental concerns [2].

Lignocellulosic biomass has diverse potential for value-added chemicals like biofuels, platform chemicals and materials production just because of dissimilarities in their compositions. The cellulose and hemicellulose are the two main carbohydrates present in LCB and are strongly bound with lignin making a complex and recalcitrant structure (Fig. 1). This complex structure is highly strong and resistant to depolymerization, therefore demands an effective pretreatment process to break the recalcitrance and avail the sugars for further processing steps [3–6]. The fractions of lignin, cellulose, and hemicellulose may differ with the type of plant and even at species level too. Plants of same species growing in different geographical locations and seasons may have different fractions of their chemical constituents. Even the harvesting time may also contribute the difference in biochemical composition [7, 8]. This compositional variation in biomass suggests that a pretreatment method may suite or not for a particular biomass, and may require further optimization and standardization studies to scale up the process [9].

Pretreatment is the primary step posing crucial role in the economic viability of the overall bioconversion of LCB [10, 11]. A recent study has estimated the cost linked with the pretreatment process of LCB around 70–150 US dollars per ton of biomass [12]. The selection of pretreatment method and its conditions are highly dependent on the type and the chemical composition of the biomass. In the last few decades, a large number of pretreatment methods have been developed and validated for different types of LCB. These methods are broadly categorized under physical, chemical, physico-chemical, and biological methods [11]. For economic feasibility of any pretreatment method the energy and solvent requirements, depolymerization, conversion of lignocellulose, generation of inhibitory compounds, losses in terms of fermentable sugars should be taken into consideration. In addition to above requisites, the pretreatment method should be simple in operation and possesses minimum cost of operation and capital cost. Considering above points, the physical, chemical, and physico-chemical pretreatment methods are most likeable as compared to biological methods [13]. Since biological methods can incur higher costs compared to other pretreatment approaches. The higher cost and potentially lower productivity associated with biological methods and depends upon the type of biomass and specific process chosen for lignin fractionation. However, it is worth noting that biological pretreatment remains highly popular for anaerobic digestion [14, 15].

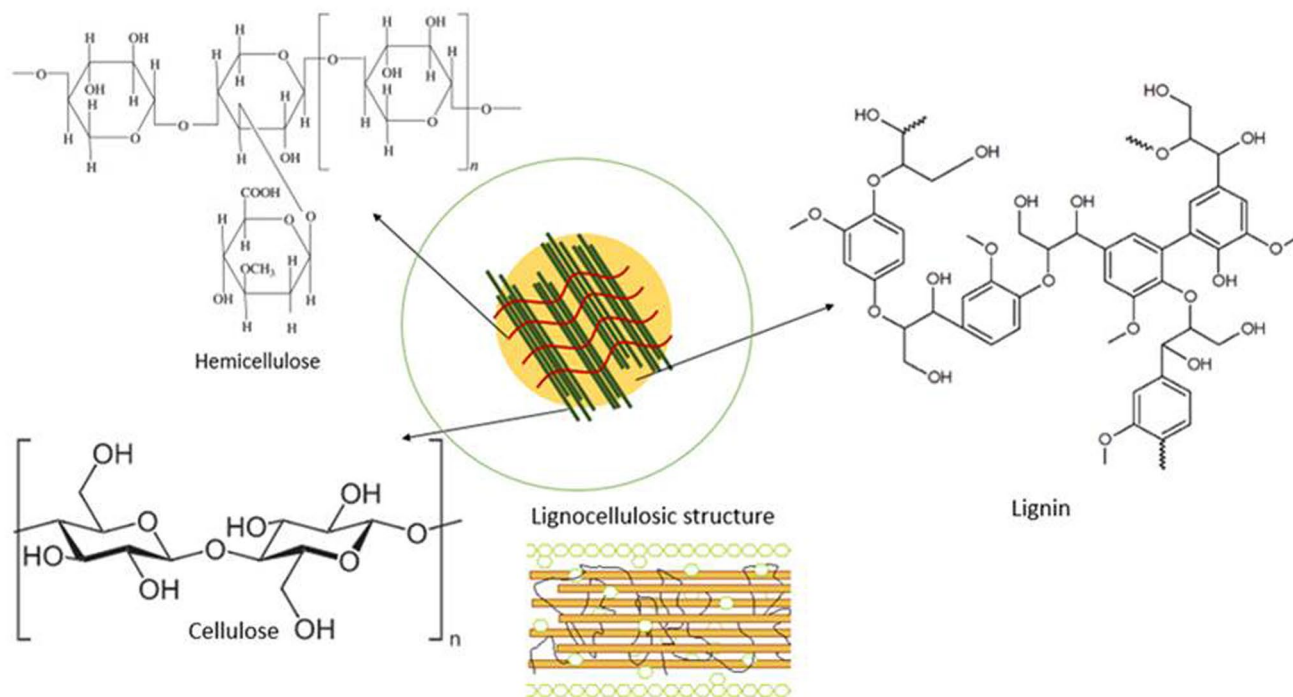


Fig. 1 Structure and major components of lignocellulosic biomass

Biorefinery and Pretreatment: At a Glance

The biorefinery is a sustainable model that facilitates the usage of underutilized renewable natural biomass to replace the wide range of non-renewable fossil-based products and also focuses on minimizing the waste generation. The utilization of waste LCB especially agricultural residues as feedstock for biorefinery has great potential to bring down negative socio-economic and environmental impacts of linear petroleum economy. It is noteworthy that LCB do not demand additional crop land, thus have no adverse effect on the human or animal food economies [16]. However, a pretreatment method is an essential necessity to fractionate the biomass into its chemical constituents that can be further processed to liquid biofuels, biogas, biofertilizer, biopesticide, antimicrobial agent, cement composites, bioplastic, paints, coatings, resins, lubricants, single cell protein, animal feed, industrial enzymes, organic acids, carotenoids, xylose, xylitol etc. through biorefinery approach (Fig. 2). Pretreatment is recognised as the second most expensive processing step after downstream processing in bioconversion of LCB to biofuels and other value-added products generation. It has been estimated that about 20% of overall LCB processing cost is being incurred by pretreatment methods. A versatile pretreatment should fulfil the desired goals viz., (i) The possibility to use high solid (biomass) to liquid concentration, (ii) Should disintegrate the lignocellulosic structure by disrupting its structural bonds, (iii)

Avoid the size reduction of biomass particles and inhibitors generation, (iv) Production of highly digestible solids to enhances enzymatic saccharification, (v) Fewer or no loss of carbohydrates (hemicellulose fraction must be preserved), (vi) Disrupt the lignin polymer and increase of surface area, (vii) Break the cellulose crystallinity and enhance the porosity of cellulose, (viii) Degradation of lignin polymers and partial depolymerization of hemicellulose, (ix) Allow the recovery of lignin fraction for reconstruction of valuable products, (x) Operation in reasonably sized and moderately priced reactors, and (xi) To be cost effective with low energy and power requirements. Previously, numerous pretreatment methods have been developed and employed for valorisation of various LCB (Fig. 3). They are encouragingly utilized to fractionate the LCB into intermediates for variety of industrial sectors like food, paper; they may substitute petroleum or may have new functionalities or better properties than the traditionally manufactured products such as: liquid biofuels [17]; chemicals like furfuraldehydes [18], 5-hydroxymethyl furfuraldehydes (HMF) [19], 2,5-furandicarboxylic acid [20], g-valerolactone (GVL) [21, 22], polymers [23, 24] and organic acids [25–29]; carbon fiber, adhesives, additives, dispersants [30–35]; and biogas [36, 37]. However, most of the existing pretreatment processes have several limitations such as sparse separation of holocellulosic and lignin complexes, elevated utilization of catalysts and/or energy, and liberation of by-products that inhibit successive conversion steps.

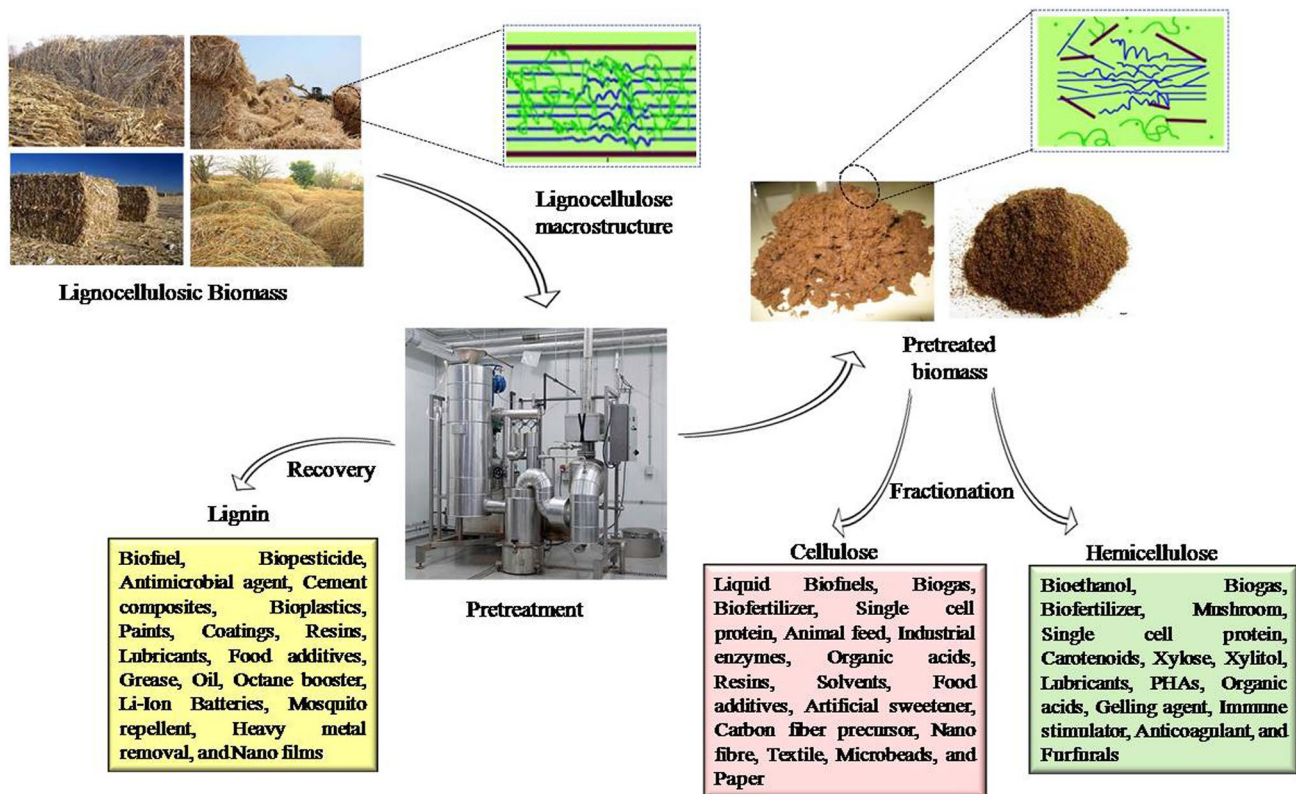


Fig. 2 Assessments of pretreatment process to fractionate the lignocellulosic biomass into various value-added products

Physical Methods of Pretreatment: Decisive But Cost Intensive

Physical pretreatment avoids the addition of chemicals, enzymes or microorganisms during the pretreatment processes thus minimize the liberation of by-products and inhibitors for successive processes. Instead, physical pretreatment methods utilize the application of temperature, pressure, and mechanical force to obtain a smaller particle size and alter the lignocellulosic structure without modifying the chemical compositions of the component. Generally, physical treatments increase the porosity and the surface area of biomass. Physical pretreatment helps in reducing the crystallinity and degree of polymerization of cellulose present in biomass [38]. The physical methods include mechanical extrusion, milling, microwave assisted methods, ultrasound, pulsed electric field etc. (Table 1). Some common drawbacks of physical pretreatment methods include: inability to remove sufficient amount of lignin, high energy and capital-cost investment, and limited information about the mode of action prohibiting its large-scale implementation. Nevertheless, physical pretreatment methods are often essential step employed prior to subsequent chemical or biochemical processes.

Mechanical Extrusion

Methods like mechanical extrusion are well known to produce char and gaseous products. The LCB treated at 50–200 °C in combination to shearing and mixing to remove and shorten the biomass fibers [39]. Zheng et al. (2014) applied the mechanical extrusion using modified twin screw extruder to remove the xylose from steam exploded corncobs at 205 °C, which resulted in structural variation and enhanced glucose from 41 to 66% depending on different extrusion parameters. Optimization of extrusion method can be done by varying the operating temperature, screw speed and depend upon the cellulose content present in biomass (Table 1) [40]. A comparative study to elaborate the effect of mechanical extrusion on switch grass, blue stem, and prairie cord grass reported the glucose yield of about 28%, 66%, and 49% with screw speed of 200 rpm, 200 rpm, and 150 rpm and at 75 °C, 150 °C, and 100 °C temperature, respectively [41]. The mechanical extrusion method utilizes high amount of operational and energy cost, which makes it unsuitable for scale up to commercial setup [42].

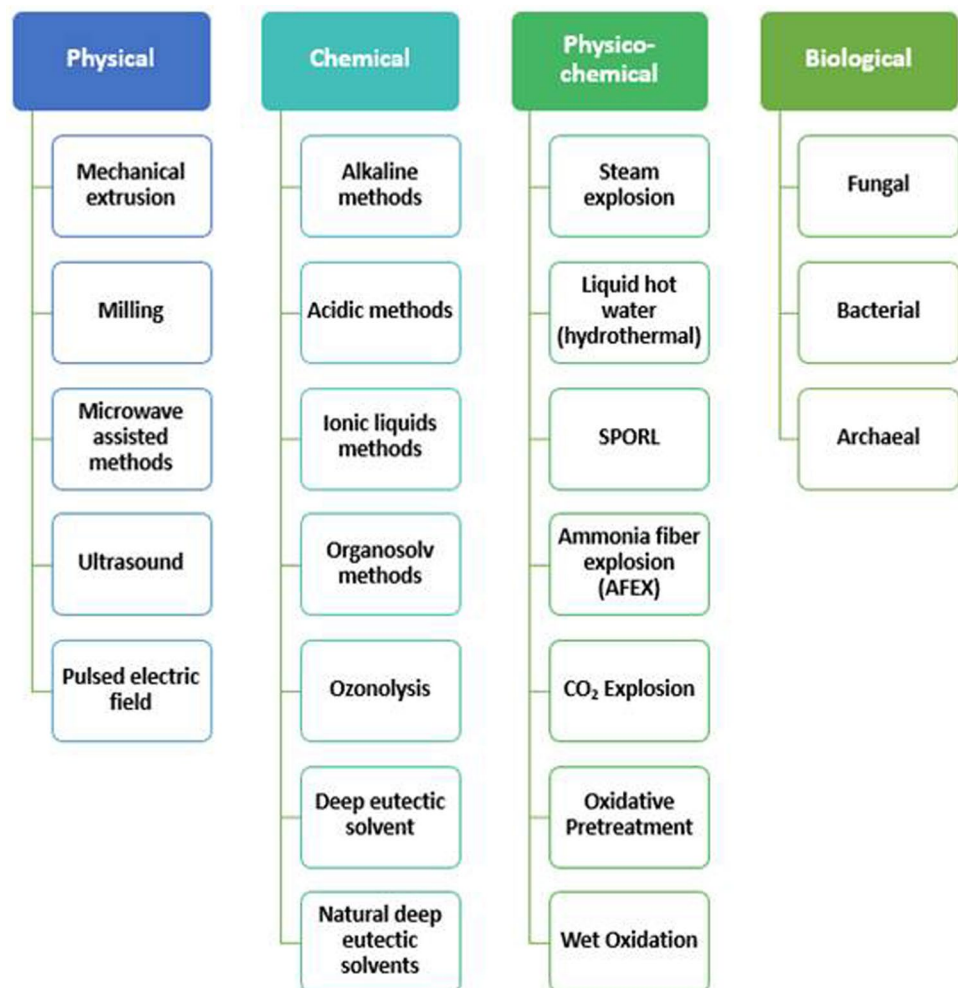
Milling Pretreatment

The mechanical size reduction is generally recognized as a first type of physical pretreatment, where the biomass is subjected to various mechanical pretreatment processes to obtain smaller particles with a given size distribution. This size reduction of biomass triggers the mass and heat transfer for subsequent pretreatment steps. Coarse size reduction, hammering, shredding, chipping, grinding, and milling are several types of mechanical size reduction processes employed in biomass conversion route (Table 1). The selection of the milling process usually depends up on the moisture content of the biomass. Generally, two-roll mills and knife mills are used for dry biomass having moisture content to about 10–15% (wet basis), whereas colloid mills are suitable for wet biomass having moisture content more than 15–20% (wet basis). Comparatively, vibratory ball milling is a much advance method than an ordinary milling process in transforming cellulose crystallinity and magnifying biomass digestibility. Disk milling is recognized as a popular mechanical pretreatment which enhances the cellulose

digestibility by producing fibres in comparison to hammer milling which produces finer bundles. On the other hand, the wet disk milling demands lower energy consumption over other traditional milling processes. Wet disk milling demands lower energy consumption and delivers efficient particle breakage, heat dissipation, reduced wear and tear of the milling equipment, improved process control (milling time, rotational speed, and concentration of the liquid medium), and increased throughput facilitated by the liquid medium [43]. According to an estimate, wet disk milling is 30% more energy efficient than dry milling methods [44].

The native complex structure of cellulose i.e. crystallinity and degree of polymerization should be modified by milling to make it more amenable to further processing. Cellulases are responsible for the hydrolysis of cellulose, but can only perform best when substrate is accessible for the enzymes. The accessibility of substrate to the enzymes can be enhanced by increasing surface area, porosity and decreasing crystallinity. Hence, milling of the biomass should be done prior to hydrolysis to increase the surface area and porosity of biomass and to decrease the crystallinity

Fig. 3 Classification of pretreatment methods employed for the delignification of various lignocellulosic biomass



and degree of polymerization of cellulose. For the milling of wet biomass colloid mill, dissolver and fibrillator are mostly used, while for dry biomass hammer mill, extruder, cryogenic mill and roller are most suited [45] whereas ball milling can be performed for both the types of biomass. The reduction in particle size up to a certain limit is beneficial for the successive chemical and enzymatic pretreatment. The particle size in finishing biomass is dependent on the nature of physical pretreatment applied. Harvesting and pre-conditioning steps transform the wood stub and logs to coarse sizes of 10–45 mm, chipping can reduce the particles size to about 5–25 mm, and grinding/milling lowers the feedstock size to 0.4–2 mm [36]. It has been demonstrated that reduction in the particles size beyond 0.4 mm has no substantial impact on hydrolysis yields of lignocellulose, however it is mainly depends upon the type of biomass and subsequent processing techniques [46]. Biomass pretreatment with ball mill is cost expensive with respect to energy consumption, which is unfavorable for the industrial scale application. The ball milling method is also incapable of delignification, which makes it undesirable for enzymatic hydrolysis which requires higher accessibility/porosity to the substrate. The changes in crystallinity, degree of polymerization and surface area are highly dependent upon the type of biomass, milling method and on the duration of pretreatment [47–49].

Microwave Assisted Pretreatment (MWAP) Methods

During the last few years, microwave assisted methods for pretreatment of LCB have received more research attention. The fractionation of composite LCB during MWAP is a result of molecular collisions possessed by dielectric polarization. The MWAP methods are studied under two categories namely, atmospheric and high-pressure treatment. Comparatively, the high-pressure microwave treatments are performed at an elevated pressure and temperature (150–250 °C) in a closed reactor. Significant increase in bioethanol yield has been reported by several researchers using MWAP methods (Table 1). These methods are being employed progressively from lab to pilot scale [50]. The MWAP methods confer the advantages of lower activation energy of the reaction and short duration of reaction, which makes them suitable pretreatment method for LCB [51]. The recalcitrant structure of the biomass breaks down when heated under microwave as the irradiation penetrates inside the rigid structure of LCB [52, 53]. The recent scientific advancements in the area of MWAP were more focused on the design of novel microwave reactors for better biomass handling to enhance the scalability [50, 54].

The use of microwave irradiation in combination to other pretreatment method has been proven to a positive strategy for efficient degradation of LCB. It has been demonstrated that combination of mild alkali reagent (NaOH at

different loadings 0.05–0.3 g/g biomass) with microwave pretreatment yielded a high concentration of reducing sugars (70–90%) [55]. Similarly, Nomanbhay et al. (2013) reported that microwave (180 W for 12 min) assisted alkali (NaOH 3% w/v) pretreatment increased the enzymatic hydrolysis to 5.8-fold from oil palm empty fruit bunch, in comparison to microwave pretreatment alone [56]. MWAP method using glycerol was found suitable to enhance the fermentable sugar yield from corncob along with eliminating the use of alkali metals [57]. Similarly, calcium chloride mediated microwave treatment enhanced the hemicellulose removal to 85.90% consequently specific surface area was increased to 168.93% as compared to untreated corn stalks [58]. In a recent study using maize distillery stillage, the high yield of enzymatic hydrolysis (75.8%) along with high sugar concentration (104.4 mg/g dry weight) were obtained with very low inhibitory compound formation [53].

Ultrasound Pretreatment

The effects of ultrasound pretreatment method on LCB have been explored for delignification and to reduce the recalcitrance of LCB to make it more accessible towards enzymatic hydrolysis (Table 1). The severity of the ultrasound pretreatment depends upon the frequency of the ultrasound waves, solvent used and on the type of reactor used [59].

The ultrasound based pretreatment methods work on principles of delignification and surface erosion. The benefits, it implies are: small pretreatment duration, lower heating requirement and use of lesser chemicals [60]. Increased biomethane production was reported using grape pomace when it was pretreated with ultrasound at 50 kHz and 25 °C for 40–70 min [61]. Chang et al. (2017) studied the effect of ultrasound in combination with ionic liquids along with SDS on the production of fermentable sugars. They observed that production of fermentable sugars, cellulose hydrolysis, and lignin removal were enhanced by 72.23%, 58.74%, and 21.01%, respectively as compared to ultrasound plus ionic liquid pretreatment. They further reported the increased delignification efficiency and decrease in cellulose crystallinity when SDS was added [62]. Saratale et al. (2020) developed an ultrasound assisted alkaline (NaOH) pretreatment method and were able to achieve 70% delignification of wheat straw and up to 84.5% hydrolysis yield along with 90% glucose and 65% xylose yield after enzymatic hydrolysis. The efficacy of the combined pretreatment method was significantly higher as compared to alkali (NaOH 2% w/v) and ultrasound (20 kHz for 30 min) treatments applied individually. The physicochemical analysis of biomass revealed that ultrasound assisted alkaline pretreatment method can break complex ultrastructure of LCB allowing enzymes to access the greater surface area of biomass [63]. Another study using ultrasound with 4% alkaline potassium permanganate for the

Table 1 Comparative analysis of different physical pretreatment methods

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Mechanical extrusion pretreatment				
Twin screw extrusion	Maize straw	Temp.: 140 °C Screw speed: 70 rpm Moisture content: 25%	Increase in biogas and methane production: 7.5% and 8.51% respectively	[67]
	Corn stover	Barrel Temp.: 120 °C Screw speed: 100 rpm Moisture content: 25% Feeding rate: 2 kg/h	Glucose yield increase: 25 g/L to 45 g/L Xylose yield increase: 19 g/L to 40 g/L Hydrolysis time reduction: 48 h to 24 h	[68]
	Vine trimming shoots	Residence time: 55 s Biomass feeding rate: 200 g/h Water feed rate: 179 g/h	Methane production increase (sequential extrusion and enzymatic hydrolysis) by: 40%	[69]
Milling pretreatment				
Ball milling	Douglas fir residuals	Rotation speed: 270 rpm Rotation ratio: 1:2 Milling time: 30 min	Cellulose crystallinity decrease: 11.7% Glucose yield: 59.67% Xylose/mannose yield: 23.82%	[70]
Ball milling + rumen fluid digestion	Rice straw (rumen-digested residue (DR))	Milling speed: 750 rpm Time: 120 min	Ethanol yield for 10% DR: 147.42 mg/g	[71]
Attritor-type laboratory ball mill	<i>Phragmites australis</i> straw	Rotor revolution rate: 600 rpm Time: 20 min Temp.: 180 °C	Non-diffusional removal of lignin with heating promoting preliminary redistribution of lignin in cell walls	[72]
Vibration ball milling	Corn stover	Volume ratio: 1:2 Temp.: <30 °C Milling time: 120 min	Decrease in cellulose crystallinity: from 42.62–10.4% Ethyl levulinate yield increased: from 36.16 mol% to 44.59 mol%	[73]
Rod milling	Wheat straw	Temp.: <30 °C Milling time: 30–240 min	Cellulose crystallinity decrease: from 51.3–11.6% Increase in specific surface area and pore volume	[74]
Microwave pretreatment				
Microwave alone	Maize distillery stillage	MW Power: 300 W Pressure: 54 psi Time: 15 min	Max. Glucose conc. achieved: 104.4 mg/g Enzymatic hydrolysis yield: 75.8%	[53]
	Brewer's spent grains (BSG)	MW Power: 1800 W Temp. 192.7 °C Time: 5.4 min	Hemicellulose sugar recovery: 64% Glucose recovery: 70% Butanol conc. achieved: 8.3 g/L Overall Butanol yield: 46 kg/t BSG	[75]
	Kitchen waste	S/L ratio: 1:5 MW intensity: 19.2 W/g Time: 6 min	Reducing sugar yield: 0.721 g/g TS Ethanol yield: 0.344 g/g TS (52% increase)	[76]

Table 1 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Microwave + CaCl ₂	Corn stover	MW Power: 800 W CaCl ₂ : 62.5% (w/w) Temp.: 162.1 °C Time: 12 min S/L ratio: 10% (w/v)	Hemicellulose degradation: 85.90% Increase in specific surface area: 168.93% Decrease in CRI: 13.91% Enzymatic hydrolysis ratio of cellulose: 90.66% Glucose recovery: 65.47%	[58]
Microwave + Ionic Liquid	Eucalyptus sawdust	MW Power: 375 W [TBA][OH] conc.: 12.5% Time: 6 min	Sugar yield: 410.67 mg/g	[77]
Microwave + Glycerol	Corn cob	Frequency: 2.45 GHz MW Power: 150 W Time: 18 min Corn cob/glycerol ratio: 1:8	Increase in levoglucosan yield: 189 times more than raw corn cob	[57]
Microwave + Binary solvent	Poplar wood	MW Power: 400 W Temp.: 120 °C Time: 10 min methanol/ dioxane	Glucan conversion by enzymatic hydrolysis: Over 99%	[78]
Microwave + FeCl ₃ + H ₃ PO ₄	Rice straw	MW Power 700 W FeCl ₃ conc.: 250 mM H ₃ PO ₄ conc.: 3% Temp.: 155 ⁰ C Time: 20 min	Maximum saccharification for pulp and biomass (48 h incubation): 98.9% and 66.4% respectively	[79]
Microwave + KCl + H ₃ PO ₄	Rice straw	MW Power: 700 W KCl conc.: 300 mM H ₃ PO ₄ conc.: 3% Temp.: 155 ⁰ C Time: 10 min	Maximum sugar yield: 30.6% Maximum ethanol yield: 12.2 g/L	[80]
Microwave + Hydrotropic extraction	Maize stillage biomass	MW power: 300 W Biomass conc.: 5% Pressure: 117 psi Time: 30 min Hydrotropic extraction: Sodium cumene sulfonate conc.: 20% (v/v)	Delignification: 44% Ethanol conc. achieved: 40 g/L Fermentation yield: 95% of theoretical yield	[81]
Ultrasound pretreatment				
Ultrasound alone	Grape pomace	US Frequency: 50 kHz US Power: 60 W Solid loading: 50 g/L Temp.: < 25 °C Time: 70 min	Increase in biomethane potential: 10% Increase in hydrolysis constant: 35%	[61]
	Microalgae (<i>C. sorokiniana</i>) biomass	US intensity: 0.35 W/mL Exposure time: 20 min	Ethanol yield: 47.84 g/L	[82]
Ultrasound + NaOH	Wheat waste biomass	US Frequency: 20 kHz Time: 30 min NaOH: 2% w/v	Delignification: 63% Hydrolysis yield: 77% Glucose yield: 86% Xylose yield: 62%	[63]
Ultrasound + KMnO ₄	Spent coffee waste	S/L ratio: 1:10 US frequency: 47 kHz US power: 310 W Temp.: Room Temp. Time: 20 min KMnO ₄ conc.: 4%	Cellulose recovery: 98% Maximum delignification: 46% Increase in reducing sugar yield after enzymatic hydrolysis: 1.7 fold	[64]

Table 1 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Ultrasound + Ionic liquid + SDS	Water hyacinth	US Frequency: 20 kHz Power: 100 W Temp.: 133 °C Time: 45 min 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) SDS: 0.5%	Increase in production of reducing sugars: 72.23% Cellulose conversion: 30.51% Delignification: 70.05%	[62]
Ultrasound + NaOH + CaO	Corn stover	US frequency: 40 kHz US power: 150 W S/L ratio: 1:20 (w/w) NaOH: 2% CaO: 6% Temp.: 50 °C Time: 30 min	Lignin conversion: 60% Increase in cumulative biogas production: from 330 to 510 mL/g-TS (54%)	[83]
Two stage ultrasonic + dilute acid pretreatment	Sugarcane bagasse	First stage US US power: 760 W Time: 20 min Second stage US with Dilute H ₂ SO ₄ US power: 190 W Time: 60 min Solid loading: 6% H ₂ SO ₄ conc.: 2% Temp.: 90 ⁰ C Time: 2 h	Delignification: 57.41% Cellulose recovery: 95.72% Hemicellulose degradation: 92.4% Ethanol fermentation efficiency: 93.37%	[84]
Pulsed electric field				
Pulsed electric field alone	Maize silage	Pulse frequency: 10 kHz Pulse duration: 50 μs Time: 180 s	Increase in biogas production: 15%	[85]
	Pig slurry	Pulse frequency: 1.7 Hz Pulse width: 4 μs Intensity: 50 kWh/m ³ Temp.: 25.3 °C	Methane production increased by: 58% COD removal increased by: 44%	[86]
	Grape pomace	Energy input: 153 kJ/kg Temp.: <5 °C	Increase in methane content by: 4% Increase in hydrolysis constant by: 14%	[61]
	Rapeseed straw	Electric pulse: 40 kV Pulse width: 50 μs Time: 5 min	Increase in methane production: 14% Increase in biogas production: 15%	[87]
	Corn cob	Electric field strength: 9 kV/cm Time: 60 s	Increase in cellulose content by: 40.59% Decrease in hemicellulose content: 12.9% Decrease in lignin content: 2.02%	[88]
Pulsed Electric Field + Enzyme hydrolysis	Rice straw	Electric field strength: 12 V/m Supplied water content: 5 mL/g substrate Enzyme loading: 26.68 mg/g substrate pH: 4.5 Switchover time: 6 h	TRS yield: 506.6 mg/L Enzymatic saccharification efficiency: 22.8%	[89]

pretreatment of spent coffee waste reported the maximum cellulose recovery of 98% with 46% delignification and an increase of 1.7-fold reducing sugar yield was observed after enzymatic hydrolysis as compared to spent coffee waste pretreated with KMnO_4 alone [64].

Pulsed Electric Field (PEF) Pretreatment

Pulsed electric field is an emerging pretreatment technology that utilizes high voltage (0.1–100 kV/cm) exposure to the LCB for very short pulse duration of nanoseconds to milliseconds. This is carried out by a device carrying two electrodes which are inserted into the biomass/biomass-suspension. The exposure of the pulsed electric field to the LCB disrupts the structural components of biomass, causing an increase in permeability and hence facilitating the access of enzymes to the carbohydrate and lignin (Table 1) [65]. PEF is generally recognized as an energy efficient method to induce permeabilization of cellular components, while it has also been proposed as a novel stress promoter, capable of inducing the production of bioactive compounds. The electric pulses in the form of square or exponential waves are used for this pretreatment method. The setup of pulsed electric field consist of a pulse generator, a control system, data acquisition system and material handling vessel [45, 66]. This technology is at incipient stage, there are still significant room exist for the improvement in fractionation capability, for example, utilizing a combination of PEF method with organic solvent/salts may achieve higher yield.

Chemical Methods of Pretreatment: The Industrially Oriented Process

Chemical pretreatment methods utilize the application of special chemicals to destruct the rigid structure of LCB. In comparison to biological and physical pretreatment methods, chemical processes are employed more frequently because they are more effective to dissolve the complex lignocellulose. They are mostly operated at atmospheric pressure and across a range of ambient temperature employing oxidizing, acidic or alkali reagent. These chemicals are responsible to disrupt the intra- and inter polymer linkages of main organic components which in turn facilitate the hydrolysis of polymeric structure and degradation of lignin units [90]. Compared to other pretreatment methods, the chemical methods are considered to be very promising, since it can be quite effective in degrading more complex LCB and has incredible potential for upgrades in efficiency [91]. A range of chemical pretreatment methods were devised by different researchers till date for the fractionation of diverse LCB. These chemical pretreatment strategies have been proved to

be effective on variety of LCB but in case of softwoods the yield of sugars is low. The chemical pretreatment processes are mostly performed utilizing alkali, acid, oxidizing agents, ionic liquids, and organic solvents to improve the biodegradability of LCB (Table 2).

Alkaline Pretreatment Methods

The alkaline pretreatment methods are more selective to delignify the biomass without disturbing carbohydrate content as much, though some amount of hemicellulose may also solubilize. Several strategies being followed by different researchers, focused on using different alkaline reagents like sodium hydroxide, calcium hydroxide, lime, ammonium hydroxide etc. (Table 2) [7]. Alkaline pretreatment of LCB can be carried out at ambient temperature for a residence period varying from few minutes to number of days and depending upon the type of alkali and lignin content [66]. Generally, alkaline pretreatment involves the alkali concentration between 1.0 and 8.0% and 90–220 °C temperature for a shorter residence time (5–100 min), or a dilute alkali concentration (0–2%) for several hours at 50–100 °C. The alkali processes affect the cellulosic residues by swelling mechanisms leading to a decrease in the crystallinity and degree of polymerization, subsequently improve the convenience of enzymes towards cellulosic fraction. It is effective in increasing the porosity and surface area accessible to enzymes of LCB, and hence improves the enzymatic hydrolysis of the biomass. These advantages make the alkaline methods suitable for the pretreatment of LCB [92, 93]. However, there are some major drawbacks associated with these methods such as longer reaction time which may vary from hours to days, high downstream processing cost required for recycling of salts, high post pretreatment cost involved for the neutralization of slurry, inability to fractionate the feedstocks with high lignin content, and sometimes adverse impacts on environment as well [94].

Alkaline pretreatment methods in combination to other chemical and physical pretreatment methods are getting much interest as the pretreatment efficiency and further hydrolysis can be significantly improved by doing so. A recent study conducted with NaOH/Urea with high biomass loading shown an increase of 31.89% in reducing sugar conversion as compared to untreated biomass. Further, FTIR and XRD analysis of cold NaOH/Urea pretreatment with 100% (w/v) biomass loading demonstrated effective disruption in lignin along with cellulose crystalline structure [95]. You et al. (2019) devised a cost effective pretreatment method (NaOH with CaO assisted by ultrasound), and were able to increase the lignin breakdown up to an extent of 60% and biogas production of more than 500mL per gram of total solid content of corn stover [83]. Another study optimized the combined effect of aqueous ammonia

and ozone and found that biogas production from rice straw can be increased by 114.2–172.8% after 90 min ozonation and 9 h soaking in aqueous ammonia [96]. Chaudhary et al. (2012) observed 85% yield of reducing sugars from *Saccharum spontaneum* after aqueous ammonia pretreatment (soaked in 30% ammonia at 10% biomass loading for 40 days at 30 °C) followed by an acid hydrolysis (H₂SO₄ 60% (v/v), 10% biomass loading at 30 °C for 4 h) process [8]. The advantage of ammonia based methods is that the ammonia can be most easily recovered and reused for further pretreatment [8]. Chundawat et al. (2020) reported a method using ammonia-salt based pretreatment at low temperatures, which decreased the cellulolytic enzyme requirements approximately by 50-fold [97].

Acidic Pretreatment Methods

Application of acids for the pretreatment of LCB is widely accepted especially in case of ethanol production (Table 2). During acid pretreatments, the hemicellulose present in biomass solubilizes in majority and a little extent of delignification takes place, this causes the increase in porosity of biomass [98]. Acid pretreatment methods are also capable of disrupting the lignocellulosic structure by cleaving interactions namely van der Waals forces, hydrogen and covalent bonds leading to the conversion of polymeric carbohydrates to oligomer sugar and monomer sugars [93, 99]. Phosphoric, acetic, sulfuric and hydrochloric acid are most commonly used acids for acid pretreatments [100]. The effectiveness of these methods depends upon the reaction time, temperature, concentration of acid, and biomass loading [99]. The major advantages of these methods include the use of highly commercial acids such as organic and inorganic acids, commercial level flexibility, greater hemicellulose removal and larger glucose yield. While the disadvantages associated are heavy cost of acid recovery, requirement of acid resistant vessels and equipment's, and inhibitory/toxic compounds formation [93, 99]. However, it is important to know that in last two to three decades the economic and environmental aspects of the acid pretreatment methods have been greatly improved with time [93, 99].

Acidic pretreatment methods are studied under two categories (i) dilute acid pretreatment (ii) concentrated acid pretreatment. The dilute acid pretreatments (0–5% w/w) are generally performed at high temperature (120–210 °C) for a long residence time (5–30 min), whereas concentrated acid pretreatments (30–70% w/w) are carried out at low temperatures (< 100 °C) for long duration (30–120 min). The dilute acid pretreatment has high reaction rate and sugar conversion, but the energy required for the overall process is higher due to the higher temperature. Whereas, concentrated acid pretreatment requires relatively lower energy consumption, but the higher acidity leads to generation of fermentation

inhibitors viz., furfurals, HMF, phenol derivatives, and aldehydes due to undesired degradation of carbohydrates. It has been estimated that the presence of these inhibitory compounds enhances the processing cost of the feedstock, ranging from 0.02 to 1.10 US dollars per kilogram of feedstock [12].

The dilute acid pretreatments are preferred, but harsh conditions of temperature and pressure are maintained for maximum recovery of fermentable sugars from LCB [101, 102]. Several variations have been made to search out the best operating parameters of acid pretreatment methods in terms of techno-economic and environmental aspects. These variations include the reactor configurations, operating conditions, severity factor etc. [99]. Among these parameters one of the most important parameter is combined severity factor (CSF) for low acid concentration, used to express the efficiency of the reaction parameters like temperature (T in °C), pH, reaction time (t in min), as given in the equation below [103, 104].

$$CSF = \log \left(t \times \exp \left(\frac{T - T_g}{14.75} \right) \right) - pH$$

Where T_g is reference temperature (100°C) and pH is the initial pH value of reaction mixture.

Tang et al. 2021 explored the effect of dilute sulfuric acid in combination with humic acid (a natural surfactant) on pretreatment of waste wheat straw and were able to achieve 40.6% delignification and 96.2% hemicellulose removal, resulting in 92.9% enzymatic hydrolysis efficiency [105]. Pretreatment of *Eucalyptus urophylla* with GVL/H₂O solution (4:1, v/v) containing 100 mM H₂SO₄ at 120 °C for 60 min, the highest glucose yield of 89.1% was achieved, furthermore 16.5% high purity lignin was also fractionated and could be used for its valorization applications [106].

Ionic Liquids Pretreatment Methods

Ionic liquids (ILs) have gained considerable attention recently for lignocellulosic biorefinery due to their recyclable capabilities. Their high solvation capabilities towards LCB leading to high yield of lignin free fermentable sugars make them promising candidate for future biorefinery platform [107, 108]. Ionic liquids are highly thermostable and possess low toxicity and work well at even low vapor pressure. They are highly selective in removing lignin and hemicellulose from LCB, yielding pure cellulose for subsequent hydrolysis process (Table 2) [4]. The main challenges with ionic liquid pretreatment are the complex processing, pH compatibility, toxicity, and higher costs involved [109]. Attempts have been made to synthesize low cost, environment friendly ILs using lignin and hemicellulose derived compounds such as [FurEt₂NH][H₂PO₄], [VanEt₂NH]

Table 2 Comparative analysis of different chemical pretreatment methods

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Alkaline NaOH	Energetic willow	NaOH conc.: 4% Temp.: 80 °C Time: 3.75 h	Delignification: 50.1% Hemicellulose removal: 73.2% Glucose yield: 510.6 mg/g biomass	[143]
	Wheat straw	NaOH conc.: 2% S/L ratio: 1:10 Temp.: 80 °C Time: 2 h	Glucan recovery: 89.5% Delignification: 71.8% Increase in enzymatic saccharification efficiency: 32.4%	[144]
	Corn straw	NaOH conc.: 2% S/L ratio: 1:10 Temp.: 80 °C Time: 2 h	Glucan recovery: 81.8% Delignification: 86.2% Increase in enzymatic saccharification efficiency: 14.8%	[144]
	Sugarcane bagasse	NaOH conc.: 2% S/L ratio: 1:10 Temp.: 80 °C Time: 2 h	Glucan recovery: 90.4% Delignification: 72.1% Increase in enzymatic saccharification efficiency: 61.6%	[144]
	Banana pseudo stem	NaOH conc.: 30% (m/m) Temp.: 121 °C Time: 30 min	Increase in cellulose content: 75.48% Reduction in lignin content: 7.65% Reduction in hemicellulose content: 4.38%	[145]
NaOH + Urea	Rice straw	NaOH conc.: 7% w/v Urea conc.: 12% w/v Solid loading: 100% Temp.: – 12 °C Time: 3 min	Cellulose retention: 91.27% Hemicellulose retention: 91.28% Delignification: 56.87% Reducing sugar conversion yield: 77.59%	[95]
NH ₄ OH	Oil palm trunk fiber	NH ₄ OH conc.: 8% Biomass loading: 1% (w/V) Temp.: 100 °C Time: 5 h	Conc. of extracted lignin: 64 mg/L	[146]
	Switch grass	NH ₄ OH conc.: 10% S/L ratio: 1:9 Temp.: 160 °C Time: 40 min	Glucose yield: >80% Xylose yield: >40%	[147]
NH ₄ OH followed by Ozonolysis	Rice straw	S/L ratio: 1:10 NH ₄ OH conc.: 27% w/w Temp.: 50 °C Ammonia treatment time: 10 h Ozone conc.: 35 mg O ₃ /L Ozonation treatment time: 45 min	Increase in glucose conc.: 54.48% Increase in biogas production: 172.8%	[96]
CaO	<i>Limnocharis flava</i>	CaO conc.: 1% Temp.: Room Temp. Time: 72 h	Reducing sugar yield: 28.88 g/L Ethanol yield: 6.31 g/L	[148]
KOH	Corn cob residue	KOH conc.: 15% Temp.: 700 °C Time: 90 min	Glucose yield: 91%; Lignin removal: 89%	[149]
KOH + Ca(OH) ₂	Wheat straw	KOH conc.: 2% Co-pretreatment with Ca(OH) ₂ : 1% Temp.: 250°C Time: 24 h	Cumulative methane yield: 239.8 mL/gVS; Improvement in biodegradability: from 56.37–66.1%	[150]

Table 2 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
KOH + anthraquinone + sodium lignosulfate	Wheat straw	KOH conc.: 15% Supplemented with Anthraquinone: (0.1%) Sodium lignosulfate: (2%) Temperature: 1200 °C Time: 40 min	Total sugar yield (glucose + xylose + soluble xylan): 80%	[151]
Ca(OH) ₂	Wheat straw	Ca(OH) ₂ conc.: 10% Temp.: 300°C Time: 5 days	Maximum biogas production: 565.63 mL/gVS	[152]
Ca(OH) ₂ + glycerol	Sugarcane bagasse	Ca(OH) ₂ conc. (in glycerol): 2% (w/v) S/L ratio: 1:10 Temp: 800 C Time: 2 h	Glucan yield: 52.5% Lignin recovery: 18.3%	[153]
Acidic H ₂ SO ₄	Cassava residue	H ₂ SO ₄ :0.05% S/L ratio: 1:20 Temp.: 180 °C Time: 10 min	Glucose recovery: 9.82% Xylose recovery: 58.62% Total sugar recovery: 22.08%	[154]
	Banana pseudostem	H ₂ SO ₄ :25% (m/m) Temp.: 121 °C Time: 30 min	Increase in cellulose content: 66.28% Reduction in lignin content: 31.15%	[145]
	Rapeseed straw	H ₂ SO ₄ : 1% Solid loading: 20% (w/v) Temp.: 180 °C Time: 10 min	Glucose yield: 80% Ethanol yield: 125 kg EtOH/Mg biomass	[155]
	Elephant grass	H ₂ SO ₄ : 20% (m/m) Temp.: 121 °C Time: 30 min	Glucose yield from Leaf: 89.2% Stem: 43.54% Whole plant: 76.01%	[156]
	Cotton straw,	H ₂ SO ₄ conc.: 2.28% (v/v) Temp.: 121.7 °C Time: 36.82 min	Maximum sugar conc.: 20 g/L Maximum ethanol conc.: 7.21 g/L	[157]
	Sunflower straw	H ₂ SO ₄ conc.: 3.68% (v/v) Temp.: 87.03 °C Time: 36.82 min	Maximum sugar conc.: 17.5 g/L Maximum ethanol conc.: 8.05 g/L	[157]
HCl	Agave plant	HCl: 0.5% (v/v) Temp.: 121 °C Time: 15 min	Highest reducing sugars conc.: 13 g/L No furfural and HMF compounds were detected	[158]
HCl with γ -valerolactone	Hybrid poplar	γ -valerolactone /H ₂ O ratio: 90:10 S/L ratio: 1:10 HCl conc.: 0.1 M Temp.: 100 °C Time: 60 min	Delignification: 68% Xylan removal: 80% Glucan conversion: 65%	[159]
HNO ₃	Artichoke stalks	HNO ₃ : 5% Solid loading: 10% (w/v) Temp.: 121 °C Time: 60 min	Glucose yield after hydrolysis: 89% Increase in ethanol yield by: 30%	[160]
H ₃ PO ₄	Sugarcane biomass	H ₃ PO ₄ conc.: 4.95% S/L ratio: 1:15 Temp.: 80 °C Time: 375 min	Monosaccharide yield: 48.7 g/L (98% glucose)	[161]

Table 2 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
H ₃ PO ₄ + H ₂ O ₂	Wheat straw	H ₃ PO ₄ conc.: 79.6% (w/w) H ₂ O ₂ conc.: 1.9% (w/w) S/L ratio: 1:10 (w/w) Temp.: 40.2 °C Time: 2.9 h	Cellulose recovery: 98.1% Hemicellulose removal: 98.2% Delignification: 69.2% Ethanol yield on dry biomass: 16%	[162]
Maleic acid	Cotton gin waste	Maleic acid conc.: 500 mM Solid loading: 10% (w/w) Temp.: 150 °C Time: 45 min	Saccharification yield: 686.13 g/g Ethanol conc. achieved: 18.74 g/L Delignification: 88%	[163]
Acetic acid	Switchgrass	Acetic acid conc.: 3 g/L S/L ratio: 1:10 (w/w) Temp.: 170 °C Time: 20 min	Biobutanol conc.: 8.6 g/L (yield of 0.16 g/g biomass)	[164]
	Oil palm shell	Acetic acid conc.: 8.24% S/L ratio: 1:10 Temp.: 107.3 °C Time: 30 min	Reducing sugar yield: 40.408 mg/g biomass	[165]
Ionic liquids				
[Bmim]BF ₄	Corn stalk	[Bmim]BF ₄ / water ratio: 50% (w/w) Temp.: 60 °C Time: 5 h	Enzymatic hydrolysis efficiency: 81.68%	[112]
Cholinium lysinate	Corn stover	([Ch][Lys]): solid loading: 15% Temp.: 140 °C Time 3 h	Delignification: 93% Glucan recovery: 86%	[166]
Microwave-assisted [Bmim] Cl treatment	Rice straw	S/L ratio: 1:20 (w/w) MW power: 400 W Temp.: 130 °C Time: 45 min	Delignification: 57.02% Increase in glucan conversion: 61.14%	[167]
Microwave-assisted [TBA] [OH] treatment	Eucalyptus sawdust	[TBA][OH] conc.: 12.5% Temp.: 60 °C Time: 2 h Microwave treatment: Microwave power: 375 W Time: 6 min	Sugar yield: 410.67 mg/g	[77]
[Bmim]Cl with ultrasound and surfactants	Sugarcane bagasse	Solid loading: 5% Temp.: 90 °C Time: 1 h PEG-8000 conc.: 3.33% US power: 100 W US frequency: 20 kHz US time: 60 min	Reducing sugar yield: 254 mg/g biomass	[168]
Ultrasound assisted ionic liquid-hydrochloric acid pretreatment	Rice straw	Ionic liquid: AMIMCl Biomass loading: 5% (wt) HCl conc.: 2.4% (wt) US power: 840 W US frequency: 40 kHz Temp.: 70 °C Time: 180 min	Increase in production of reducing sugar: from 20.13–28.96% Increase in cellulose conversion: from 31.69–35.23% Increase in delignification: from 18.06–19.33%	[169]
[AMIM]Cl with surfactants	Rice straw	Solid loading: 10% Rhamnolipid surfactant conc.: 1% Temp.: 110 °C Time: 1 h	Delignification: 26.14% Cellulose conversion: 36.21%	[170]

Table 2 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
[Bmim]Cl with acid	Rice straw	Aqueous [Bmim]Cl water content: 20% Solid loading: 15% HCl conc.: 0.5% Solid loadings (5–20% w/v) Temp. 130 °C Time 2 h	Cellulose digestibility: 98.8% Ethanol conc.: 21.86 g/L	[171]
Organosolv				
Ethanol	Wheat straw	Ethanol conc.: 60% Temp.: 200 ⁰ C Time: 2 h	Lignin yield: >90%	[172]
Ethanol + H ₂ SO ₄ catalyst	Eucalyptus wood	Ethanol conc.: 50% H ₂ SO ₄ (catalyst) conc.: 1% Temp.: 160 °C Time: 10 min	Glucose yield: 37.1% Hemicellulose reduction: 11.4% Lignin yield: 22.6 g	[173]
Ethanol + n-propylamine catalyst	Corn stover	Ethanol conc.: 60% v/v n-propylamine catalyst: 10 mmol/g biomass Temp.: 140 °C Time: 40 min	Delignification: 81.7% Total sugar yield: 83.2%	[174]
Glycerol + Ammonia catalyst	Sorghum	Glycerol conc.: 51.11% w/w Ammonia catalyst conc.: 5.14% w/w Temp. 120 °C Time: 1 h	Total sugar yield: 421.35 mg/g cellulose digestibility: 72% maximum ethanol conc.: 36 g/L	[175]
Glycerol + H ₂ SO ₄ catalyst	Sugarcane bagasse	Solid loading on glycerol: 1:10 H ₂ SO ₄ (catalyst) conc.: 0.06% Temp.: 200 °C Time: 15 min	Cellulose retention: 98% Hemicellulose removal: 82% Delignification: 52% Glucose yield: 70%	[176]
Acetone + H ₂ SO ₄ catalyst	Mustard straw and stalk (MSS)	Aqueous acetone: 80% v/v S/L ratio: 1:10 H ₂ SO ₄ (catalyst) conc.: 0.4% Temp.: 121 °C Time: 90 min	Cellulose retention: 58.2% Hemicellulose reduction: 15.9% Lignin reduction: 18.5% Glucose yield: 13.67%	[177]
Tetrahydrofurfuryl alcohol + H ₂ SO ₄ catalyst	Hybrid <i>pennisetum</i>	Tetrahydrofurfuryl alcohol (THFA): S/L ratio: 1:12 H ₂ SO ₄ (catalyst) conc.: 0.05 mol/L Temp.: 100 °C Time: 2 h	Enzymatic digestibility: 87.5% Glucan recovery: 90.9% Delignification: 50.3%	[178]
Binary Solvent	Poplar wood	Methanol/dioxane ratio: 75/25 (v/v) MW power: 400 W Temp.: 120 °C Time: 10 min	Delignification: 88.3% Hemicellulose removal: 70.4% Cellulose retention: 83.1% Glucan conversion: 99%	[78]
Ozonolysis				
Ozonolysis alone	<i>Eucalyptus grandis</i>	Ozone conc. 60 g O ₃ /m ³ Moisture content: 30% Time: 120 min	Reduction in lignin content: 26.63–9.53% Increase in saccharification yield: 20 to 68%	[179]
	Rye straw	Ozone conc. 100 g O ₃ /m ³ S/L ratio: 1:10 Time: 60 min Moisture content: 30%	Increase in conc. of reducing sugars, volatile fatty acids and chemical oxygen demand: 7.4, 32.3 and 11.7 times higher respectively Methane yield: 291.74 dm ³ /kg VS	[180]

Table 2 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Ozonolysis followed by thermal pretreatment	Rice straw	Ozone dosage: 0.006 g O ₃ /g biomass Time: 30 min Thermal pretreatment: Temp.: 55 °C Time: 4d	Reducing sugar yield: 1.18 mg/L/d Increase in hydrolysis rate constant: 26% Methane yield: 374 ml CH ₄ /g VS substrate	[181]
Ozonolysis + NaOH	Sugarcane straw residue	Ozone conc.: 0.24% Time: 60 min Moisture content: 35% NaOH conc.: 0.1 mol/L Temp.: 80 °C Time: 8 h	Glucose yield: 60.8% Increase in cellulose content: 75% Increase in hemicellulose content: 42% Decrease in lignin content: 47%	[123]
Ozonolysis followed by H ₂ SO ₄ treatment	Sugarcane bagasse	Ozone flow rate: 32 mg O ₃ min ⁻¹ Time: 60 min Moisture content: 50% Dilute acid washing: Biomass loading: 5% H ₂ SO ₄ (catalyst) conc.: 0.1 mol/L Temp.: 25 °C Time: 2 h	Delignification: 25% Glucose yield: 310 mg/g Xylose yield: 122 mg/g	[182]
Ozone followed by Subcritical Water treatment	Wheat bran	Ozone conc.: 60 mg/L Time: 30 min Moisture content: 50% Subcritical water treatment: Solid/liquid ratio: 1:10 Temp.: 160 °C Time: 30 min	Hemicellulose removal: 86% Glucose yield: 85%	[183]
Deep eutectic solvent (DES) Choline chloride-glycerol	Hybrid <i>Pennisetum</i>	Biomass loading: 1:10 (w/w) Temp.: 120 °C Time: 6 h	Cellulose retention: 95.2% Cellulose saccharification: 99.5% Delignification: 78.88% Hemicellulose removal: 93.63%	[137]
Choline chloride-glycerol	Rice straw	Solid loading: 5% Temp.: 150 °C Time: 15 h	Glucan retention: 96.5% Delignification: 52.3% Increase in glucan digestibility: 21–87%	[184]
Choline chloride: monoethanolamine	Wheat straw	Biomass loading: 1:20 (w/w) Temp.: 70 °C Time: 9 h	Delignification: 71.4% Cellulose retention: 93.7%	[185]
Choline chloride /glycerol followed by Ultrasound treatment	Sugarcane bagasse	ChCl/glycerol ratio: 1:10 (m/m) Biomass loading: 3% (w/w) Temp.: 121 °C Time: 15 min US power: 40 W US frequency: 20 kHz Time: 20 min	Sugar yield: 276.8 mg/g biomass Ethanol yield: 142.09 mg/g biomass	[186]
Natural deep eutectic solvent (NADES) NADES	Corn cob	Betain-amino acid biomass loading: 1:10 (w/w) Temp.: 60 °C time: 5 h	Delignification: 57.01% Glucose yield: 40.5%	[187]

Table 2 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
NADES + DMSO + Ultra-sound	Corns straw	Choline chloride/oxalic acid ratio: 1:1 Biomass to solvent ratio: 1:50 Biomass to catalyst (SnCl ₄) ratio: 2:3 Biomass to DMSO ratio: 1:20 Temp.: 140 °C Time: 3 h US frequency: 40 kHz US power: 120 W Temp.: 25 °C Time: 30 min	Increase in Yield of 5-HMF: 27.54% Furfural: 33.64% Pentose: 95.63% Hexose: 49.45%	[188]

[H₂PO₄], and [p-AnisEt₂NH][H₂PO₄] and were found effective compared to other ILs [110]. The ILs specifically recognized for the cellulose dissolution are imidazolium, pyridinium, ammonium, phosphonium or morpholinium based cations and anions. The capability of these ionic liquids to form strong hydrogen bonds with hydroxyl groups make them efficient for the cellulose dissolution [60].

Beside all the encouraging features of ILs, their commercial scale application is limited because of high viscosity, requirement of costly ionic liquids in large amounts, and negative effect of ILs on cellulases [111]. Hu et al. (2018) had overcome the problem of viscosity by adding 50% (w/w) water to the [Bmim]BF₄ ionic liquid and were able to increase enzymatic hydrolysis efficiency up to 81.68% [112]. Pretreatment of *Eucalyptus* sawdust using ionic liquid in combination with microwave increased the delignification and cellulosic crystallinity deconstruction, which in turn increased the enzymatic hydrolysis [77]. Acetate based ionic liquid along with probe sonication pretreatment method was found capable of completely dissolving the bamboo biomass in merely 40 min, showing significant reduction in time for complete LCB dissolution and considerably change in thermo-physical characteristics of regenerated cellulose rich material [113]. Recently, Chuetor et al. (2022) optimized the pretreatment conditions of rice straw using 1-ethyl-3-methylimidazolium acetate and reported 89% more ethanol production than the untreated rice straw even after five recycles of IL [114]. Such findings have inspired the researchers to utilize the various IL pretreatment methods to make the idea of biorefinery an actuality.

Organosolv Pretreatment Methods

Organosolv pretreatment strategies have been established for industrial manufacturers of pulp & paper and bioethanol [11, 115]. Organosolv pretreatment method utilizes organic solvents like ethanol, acetone, ethylene glycol, formic acid,

acetic acid, etc. for the delignification and hemicellulose solubilization (Table 2) [11]. The major advantage associated with organosolv pretreatment is that the solvent used can be recovered and reused. The organosolv methods of pretreatment are effective in fractionating LCB to its structural component: cellulose, hemicellulose, and lignin with high purity [93]. Organosolv pretreatment is in general carried out at an elevated temperature stretching from 100 °C to more than 200 °C. The acid catalysts like hydrochloric acid, sulfuric acid, oxalic acids etc. can also be used to increase the lignin extraction efficiency and in promoting hemicellulose breakdown [116, 117].

A recent study used methanol/dioxane binary solvent in addition to microwave irradiation to fractionate poplar wood into high quality cellulose, lignin, and monomeric sugar derivatives under mild condition of pretreatment i.e. 120 °C temperature for 10 min. Further, enzymatic hydrolysis of fractionated cellulose resulted in almost theoretical glucan conversion yield over 99% [78]. The high fractionation ability of organosolv pretreatment methods makes it the most encouraging biorefinery approach for meeting the objective of complete utilization of LCB without or minimal waste generation [118]. Kabakcı and Tamiş (2020) compared different organosolv solvents (ethanol, alkaline glycerol, acetic acid, and formic acid/acetic acid/water) for the fractionation at atmospheric pressure and lower temperature and observed lignin precipitation yield ranging from 6.6% in ethanol organosolv and 42% in alkaline glycerol organosolv [119].

Ozonolysis Pretreatment

Ozonolysis is an oxidation reaction which utilizes ozone, a very strong oxidising agent for lignocellulose solubilization. The ozonolysis is much selective in breaking lignin component of the LCB leaving behind the cellulose and hemicellulose minimally affected (Table 2). Lignin is highly vulnerable towards the attack of ozone because of its electron rich properties and high contents of C=C bonds [120, 121]. The

ozonolysis of lignin generates low molecular weight compounds majorly organic acids like formic and acetic acid, which results in lowering the pH of the solution up to 2. It poses several advantages over other pretreatment methods like selective delignification, milder reaction conditions, minimal inhibitory compound formation etc., while it also poses risks of fire and corrosion along with high cost of ozone generation, which limits its usage at industrial scale [122]. In a recent study, sugarcane straw was subjected to ozonolysis in different soaking media (acid, neutral and basic) and compared. The method preserved almost all the holocellulose while lignin content was reduced by 47% along with significant reduction in recalcitrance of the biomass, resulting in 60 and 71% yield of glucose and xylose respectively after enzymatic hydrolysis [123].

Deep Eutectic Solvent (DES) Pretreatment

In recent years, the development of mild and sustainable green process for industrial biorefining has got huge research attention (Table 2) [124]. Among different pretreatment methods, deep eutectic solvents are deliberately used as unique green solvents for pretreating LCB with added advantages like easier synthesis, extraordinary purity, lesser toxicity, biodegradable in nature, low melting points, high thermal stability, low volatility, non-flammability, and high air stability [125, 126], and most important they possess all the twelve principles of green chemistry [127]. Above all these DESs have outstanding competence of delignification from LCB [128–135]. The capability of delignification and hemicellulose removal from LCB during pretreatment can be determined by the ability of dissociation of protons by the DESs [136].

A recent study with DESs in addition with FeCl_3 , ZnCl_2 , CuCl_2 and AlCl_3 was used to treat hybrid Fountain grasses, the authors observed high level of cellulose retention (95.2%) and up to 99.5% cellulose enzymatic hydrolysis with DES when used with FeCl_3 [137]. Whereas, in another study a two-step pretreatment strategy was followed, which includes liquid hot water extraction prior to mild acidic DES pretreatment. Out of three acidic DES (formic-, acetic-, and lactic acid-choline chloride) for selective delignification of poplar wood, the formic- and acetic acid DES contributed similar results with 76.4 and 76.5% delignification, while acetic acid deep eutectic acid was found most selective for the delignification with selectivity index of 7.9 [138].

In recent years, Natural deep eutectic solvents (NADES) have also gained more research interest for the delignification of LCB in a biofuels production route (Table 2). NADES are basically advanced liquid salts and are generated by mixing of cheap and readily available components such as quaternary ammonium salt (cholinium chloride) and naturally occurring hydrogen bond donor like amines,

sugars, alcohols and carboxylic acids [139]. NADES offer several eco-friendly and economic advantages which include; cheaper synthesis, easy availability of components, easy synthesis, less toxicity, and high sustainability. They possess very low melting point even below 0°C , negligibly volatile, wide range of polarity, adjustable viscosity and great solubilization property for different molecules [139]. Few years back several stable NADES based on natural compounds (primary metabolites like organic acids, amino acids and sugars) were reported [140, 141]. Kumar et al. (2016) reported a method for high quality lignin and holocellulose separation in a single step from rice straw using NADESs. More than 60% delignification was achieved with greater than 90% purity of extracted lignin [142].

Physico-Chemical Methods of Pretreatment

In general, physico-chemical pretreatment methods exploits the physical properties like high temperature or pressure along with some chemicals to pretreat the LCB. Most of these methods are conducted at high temperature and sometimes with high pressure. In physicochemical pretreatment, lignin and xylan fractions of the lignocellulose are broken-down by altering the working conditions (like moisture, biomass particles size, solid loading, temperature, and pressure) in the presence or absence of a catalyst. The physico-chemical pretreatment methods include steam explosion, liquid hot water, wet oxidation, oxidative treatment, ammonia fiber explosion, supercritical carbon dioxide, sulfite pretreatment etc. These methods primarily increase the surface area for enzyme accessibility, decreases cellulose crystallinity, extract hemicellulose, and delignify biomass [5, 100]. Some recent studies on chemical pretreatment methods and their effects on further processing are summarized in Table 3.

Steam Explosion Pretreatment

Lignocellulosic pretreatment with steam explosion is a method of choice at commercial scale. Steam explosion is a potential thermochemical pretreatment method for LCB as it increases the accessibility of biomass towards the action of hydrolyzing enzymes by disrupting its structural components. This method also alters the cellulose crystallinity by dissolving the amorphous region of lignin and xylan. It affects the biomass by three actions i.e. steam heating, shearing of biomass due to sudden pressure release, and auto hydrolysis of glycosidic bonds [189]. The method employs saturated steam at high temperature (generally more than 160°C) and high pressure (more than 5 bar) for few seconds to many minutes, causing disruption of structural components of cell wall and solubilization of acid soluble lignin

and hemicellulose [93, 190]. The particle size of biomass, temperature, moisture content, solid loading, residence time, and the cumulative effect of temperature and duration (severity factor) are the main parameters affecting the efficacy of steam explosion pretreatment (Table 3). The starting material and biomass particles size determines the correlation among processing temperature and residence period. Low temperature for longer residence time has been reported better than high temperature for lower residence time treatment due to less fermentation inhibition product formation. The severity factor for steam explosion can be expressed as [191]:

$$\log R_0 = \log(t \times e^{[T-100/14.75]})$$

where, $\log R_0$: the severity factor as a function of treatment time; T: temperature ($^{\circ}\text{C}$); t: residence time (min); 14.75: activation energy where the process obeys first order kinetics and the Arrhenius temperature dependence.

The major advantage of steam explosion is that no chemicals are required and hence it is pollution free method, and it requires low energy and cheaper in recycling waste stream whereas the disadvantages account lower carbohydrate saccharification efficiency and generation of inhibitory products (like furfurals and HMF) [189].

A recent study using steam explosion in a semi continuous pre-pilot reactor for the pretreatment of switchgrass reported up to 88.3% enzymatic saccharification, which was found similar to the enzymatic hydrolysis of commercial cellulose pulp [192]. Matsakas and his team fractionated the spruce biomass using lignin first strategy. They applied hybrid organosolv-steam explosion pretreatment technology, and obtained the solid residue comprised of up to 72% w/w cellulose component and achieved 79.4% delignification. Though, the saccharification efficiency could reach only up to 61%. Furthermore, the high purity lignin is an added advantage to this method, which can be further used for high value added materials [193].

Liquid Hot Water (Hydrothermal) Pretreatment

Hydrothermal or liquid hot water pretreatment method employs the liquid water at high temperatures and high pressure to maintain the liquidity of water for the LCB. Generally, 160–240 $^{\circ}\text{C}$ temperature is maintained [60, 93, 190]. Though this method does not employ any chemical and catalyst to carry out the pretreatment, but acidic pH water at high temperature classifies the method under physico-chemical pretreatments (Table 3). The pretreatment conditions solubilize most of the hemicellulosic portion and partially delignify the LCB and make the cellulose more accessible towards hydrolysis [194]. A pH between 4 and 7 is desirable to limit the production of inhibitors and preventing

sugar degradation and loss [189]. Also as in case of steam explosion, the sudden pressure release is not required during hydrothermal pretreatment method, therefore make this process easier to operate [189].

The severity factor is one of the most important parameter for the effectiveness of hydrothermal pretreatment as well. A lower severity factor (3.39) was reported ineffective in deconstruction of sugarcane straw while severity factor greater than 4.70 causes the loss of fermentable sugars and generates inhibitors like furfural and formation of pseudo-lignin structures, although around 97% hemicellulosic removal was achieved [195]. Li et al. (2017) evaluated the effect of hydrothermal pretreatment on poplar wood and observed substantial xylan solubilization (50–77%) along with changes in lignin structure such as decrease of β -O-4' ether linkages and removal of cinnamyl alcohol end group and acetyl group [196]. The upcoming research should be focused in such a way that the maximal sugars can be recovered and with reasonable amount of hemicellulose solubilization.

Wet Oxidation Pretreatment

Wet oxidation pretreatment of LCB employs water at a temperature above 120 $^{\circ}\text{C}$ and pressure ranging from 0.5 to 2 MPa for residence period of up to 30 min. The method is efficient for the LCB having higher amounts of lignin. The major parameters affecting wet oxidation are pretreatment duration, oxygen/air pressure and temperature of reaction (Table 3). Water at elevated temperatures behaves like an acid and hence hydrolysis of biomass favors with increase in hydrogen ions with enhancement in temperature leading to lowering in pH of the reaction mixture [45]. Oxygen or air is used in this pretreatment as a catalyst [189]. This method of pretreatment generally acts upon hemicellulose leading to its solubilization and further hydrolysis into constituting monomeric sugars and delignification through decomposition of lignin in CO_2 , H_2O and carboxylic acids [197, 198]. A study using wet oxidation (6% oxygen in the form of H_2O_2) pretreatment for oil palm empty fruit bunch reported an increase of 43% in methane yield as compared to control during mesophilic conditions of biogas production [199].

Oxidative Pretreatment

Oxidative pretreatment is carried out using different oxidizing agents such as air, oxygen, hydrogen peroxide, and ozone. The mechanism of the lignocellulose breakdown depends on the oxidizing agent used and/or the pretreatment conditions [38, 65]. This method involves the oxidation which mainly results in breakdown of lignin, hemicellulose depolymerization into its constituting monomeric sugars and organic acids and the partial breakdown of

Table 3 Comparative analysis of different physico chemical pretreatment methods

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Steam explosion pretreatment				
Steam explosion alone	Switchgrass	Temp.: 200 °C Residence time: 10 min Pressure: 15 bar	Saccharification yield: 88.3%	[192]
	Beechwood	Temp. 230 °C Time 14.9 min (treatment severity 5.0)	Glucose yield: 88% Xylan recovery: 91% (from liquid)	[216]
	Rubber wood waste	Temp.: 214 °C Time: 10 min (treatment severity: 4.35)	Methane yield: 83.9 L CH ₄ /kg VS Glucan conversion: 45.2%	[217]
Steam explosion –NaOH catalyzed	Sugarcane bagasse	NaOH conc.: 0.1 M Temp. 180 °C Pressure 8.8 Kgf cm ⁻² Time: 5 min	Delignification: 65% Total reducing sugars conc.: 9.07 g/L	[218]
Steam explosion –CaO catalyzed	<i>Hippophae rhamnoides</i>	Pressure: 1.5 MPa Time: 20 min CaO loading: 2% Moisture content: 65%	Hemicellulose removal: 77.61% Enzymatic sugar yield increase: 66 mg/g DM to 300 mg/g DM	[219]
Steam explosion - H ₂ SO ₄ catalyzed followed by organosolv treatment	Spruce wood chips	H ₂ SO ₄ (catalyst) conc.: 0.5% Temp.: 225 °C Time: 5 min Organosolv treatment: Ethanol conc.: 52% Time: 30 min	Saccharification yield: 61% Cellulose retention: 72% Delignification: 79.4%	[193]
Hydrothermal pretreatment				
Hydrothermal alone	Sugarcane straw	Solid loading: 10% (w/v) Temp.: 195 °C Time: 10 min	Cellulose retention: 90.2% Hemicellulose removal: 85.45%	[195]
	Poplar wood	Solid loading: 5% (w/w) Temp.: 180 °C Residence time: 70 min	Decrease in xylan content: from 12.3–2.8% Increase in cellulose content: from 38% Reduction in lignin content: from 23.7–21.3%	[196]
	Corncoobs	Solid loading: 10% (w/v) Temp.: 160 °C Residence time: 10 min	Pentose yield: 58.8% Delignification: 60% Glucose recovery: 73.1%	[220]
	Switchgrass	Solid loading 15% (w/w) Temp. 200 °C Time 5 min	Glucan and xylan recoveries: 86% and 96% respectively hydrolysis efficiency: 89%	[221]
Hydrothermal + NaOH catalyzed	Bamboo wood	Solid loading: 10% (w/v) NaOH (catalyst conc.): 0.5% Temp. 170 °C Time 2 h	Ethanol yield: 4.8 g/L Xylan content reduction: from 18.2–12.9% BET surface area increase: from 0.324 m ² /g to 23.09 m ² /g Cellulose conversion increase: 38.3%	[222]
Hydrothermal followed by Na ₂ CO ₃ + O ₂	Reed straw	Solid loading: 10% (w/v) Temp. 170 °C Time: 60 min Carbonate oxygen pretreatment: Na ₂ CO ₃ conc.: 33.3 g/L Oxygen pressure: 0.6 MPa Temp.: 150 °C Time: 40 min	Total sugar yield: 79.1% Delignification increase: from 73.4–94.4%	[223]

Table 3 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Liquid hot water followed by DES	Poplar wood	Liquid hot water extraction: Solid/liquid ratio: 1:30 Temp.: 170 °C Time: 40 min Acidic deep eutectic solvent: ChCl: Acetic acid molar ratio: 1:2 Temp.: 130 °C Time: 3 h	Delignification: 76.5% Increase in cellulose content: from 61.1–85.4% Selectivity index: 7.9	[138]
Ammonia fiber explosion (AFEX) pretreatment				
AFEX alone	Corn stover	Water loading: 0.7 gH ₂ O/g DM Ammonia loading: 1.0 g NH ₃ /g DM Temp.: 130 °C Time: 10 min	Lignin yield: 16.55% Average molecular weight of lignin (M _w): 3925 g/mol Polydispersity index: 1.668	[204]
	Hardwood biomass	Temp.: 140 °C Time: 1 h	Glucose yield in birch and willow 53.3% and 47.6% respectively	[224]
	Sugarcane bagasse	Ammonia loading: 0.7 g NH ₃ /g DM Water loading: 0.6 g H ₂ O/g DM Temp.: 120 °C Residence time: 60 min	Specific methane yield: 299 L CH ₄ /kg VS Biogas methane content: 58%	[206]
	Distillers dried grains with solubles (DDGS)	Ammonia conc. 10% (w/v) Solid loading: 13.18% Temp.: 70 °C Time: 48 min	Total reducing sugar yield: 0.129 g/g DDGS	[225]
Supercritical carbon dioxide (Sc-CO ₂) based Pretreatment				
Sc-CO ₂	Oil palm biomass	Pressure: 35 MPa Temp.: 100 °C Moisture content: 60%	Hydrolysis yield: 42.77% Cellulose conversion: 61.14%	[226]
	Corn stover	Pressure: 22.5 MPa Moisture content: 75% Temp.: 70 °C Time: 24 h	Enzymatic hydrolysis sugar yield increase: from 15.9–46.3%	[211]
	Corn cob	Pressure: 20.0 MPa Moisture content: 75% Temp.: 70 °C Time: 24 h	Enzymatic hydrolysis sugar yield increase: from 15.9–38.2%	[211]
	Sugarcane bagasse	Pressure: 200 kgf/cm ² Temp.: 60 °C Time: 6 h	Lignin removal: 8.07% Increase in methane production: 24%	[227]
Sc-CO ₂ + Organosolv	Cotton stalk	Pressure: 100 bar Temp.: 180 °C Time: 140 min combined with organosolv (ethanol) pretreatment	Maximum methane yield: 177 L/kg _{VS}	[228]
Wet oxidation				
Wet Oxidation	Oil palm empty fruit bunch	Oxygen loading (as hydrogen peroxide): 6% Temp.: 180 °C Time: 45 min	Increase in methane yield: 43%	[199]

Table 3 (continued)

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
Aqueous ammonia wet oxidation + dilute acid pretreatment	Corn stover	Aqueous ammonia wet oxidation: NH ₄ OH conc.: 12.6% Temp.: 130 °C Time: 40 min Oxygen pressure: 3.0 MPa Dilute acid pretreatment: HCl conc.: 1% S/L ratio: 1:10 Temp.: 120 °C Time: 40 min	Glucan recovery: 71.5% Lignin removal: 86.1%	[229]
Alkaline hydrogen peroxide assisted wet air oxidation + wet air oxidation	Rice straw	Alkaline hydrogen peroxide assisted wet air oxidation: H ₂ O ₂ conc.: 0.5% H ₂ O ₂ soaking time: 24 h Wet air oxidation: Pressure: 6 bar Temp.: 190 °C Time: 20 min	Cellulose recovery: 84.31% Hemicellulose solubilization: 71.86% Lignin removal: 76.90%	[230]
Sulfite pretreatment				
Sulfite pretreatment	Oil palm trunk	Sulfite conc.: 6% H ₂ SO ₄ conc.: 7% Temp.: 190 °C Time: 30 min	Cellulose conversion: 92% Overall glucose yield: 66% Lignin removal: 38.8%	[231]
	Dairy manure	Sulfite conc.: 4% H ₂ SO ₄ conc.: 9% Power: 500 W Temp.: 180 °C Time: 20 min	Methane yield at moderate-SPORL: 353 mL/g _{VS} (75% increase)	[232]
	Sugarcane bagasse	Sulfite conc.: 6% H ₂ SO ₄ conc.: 1.1% Temp.: 160 °C Time: 30 min	Hydrolysis yield: 85.33%	[233]

cellulose increasing the cellulose accessibility towards enzymatic hydrolysis [38, 200]. It has been reported that oxidative pretreatment is not selective and generally simultaneous degradation of heteropolymeric lignin along with hemicellulose and cellulose can be observed from the lignocellulose. During oxidative pretreatment delignification occurs because of oxidation of aromatic rings to the carboxylic acid with the help of oxidant as catalyst [201]. Beside oxidation, electrophilic substitution, side chain displacement, and alkyl-aryl linkage breakdown also occurs during oxidative pretreatment [200]. Fernández–Delgado et al. (2019) compared mild alkaline and oxidative pretreatment methods for biobutanol production from brewer's spent grain and observed 62.8% glucose yield and 28.1% xylose yield after enzymatic hydrolysis. Later on after fermentation of fermentable sugars a maximum of 11.0 g/L butanol concentration along with 13.7 g ABE/L was observed [202].

Ammonia Fiber Explosion (AFEX) Pretreatment

The ammonia fiber explosion method is quite similar to the steam explosion pretreatment method in terms of operation; however, the pretreatment conditions are quite different because of volatile nature of ammonia. The digestion temperatures range between 50 and 110 °C are significantly lower in comparison to steam-explosion, therefore it requires lower energy and total investment cost [38]. The duration of pretreatment may vary from few minutes to hours depending upon the reaction temperature. AFEX pretreatment causes the swelling of biomass, disruption of structural components of the LCB, reducing crystallinity of the cellulose, increasing surface area and lignin-carbohydrate linkages disruption [93, 203]. The modified lignin structure increases the water-retention capacity; thereby facilitate the digestibility of feedstocks. AFEX pretreatment may be less effective with LCB that have high lignin content because the presence of lignin hinders the penetration and reaction of ammonia during the pretreatment process. However, AFEX pretreatment

offers the advantage of not requiring much size reduction compared to other methods, as the rapid fiber expansion facilitates effective ammonia penetration even with larger particle sizes [189]. The degree of biomass disruption can be improved by process parameters optimization viz., treatment time, blow down pressure, temperature, and ammonia and water loading (Table 3). The major advantage of using AFEX is that ammonia can be easily recovered and reused for further pretreatment purpose.

A recent study was conducted by Zhao and his team to see the synergistic effect of hydrogen peroxide and ammonia on lignin and formulated that the oxidation and ammonolysis was led by hydrogen peroxide and ammonia, respectively. The oxidation occurs at S unit of lignin whereas ammonolysis occurs at ferulate and p-coumarate esters. They observed that the combined effect of hydroxide peroxide and ammonia is highly effective in degrading lignin and reducing the polydispersity index generating homogeneous lignin fragments [204]. Wang and co-workers (2019) performed the AFEX pretreatment of corn stover to extract lignin and utilize it for the lipid production. They observed that *Rhodococcus opacus* can utilize the AFEX treated lignin without any treatment and produced lipid up to 32 mg/L in 72 h utilizing 20% of total lignin. The lipid accumulated has the same composition as of the vegetable oil [205]. Mokomele et al. (2019) compared steam explosion and AFEX pretreatment on biogas production from sugarcane bagasse and observed that AFEX pretreatment gave the highest specific methane yield along with high methane content [206]. Unlike other biomass pretreatment processes, AFEX process does not generate inhibitors; therefore, the subsequent downstream processes become more efficient. There is a wide literature available on the advantages of AFEX process which highlights the lower moisture requirement, fewer formations of inhibitory sugar by-products, 100% recovery of feedstocks material, and positive effect on enzymatic hydrolysis in comparison to other chemical methods. Besides, there are some disadvantages such as high costs due to chemicals recycling and appropriate reactors requirement still need to be overcome.

Supercritical Carbon Dioxide (Sc-CO₂) Based Pretreatment

Supercritical fluids possess the characteristics of gases and liquids. Their diffusivity and viscosity are same as of gases and density is same as of liquids [207]. The fluids at a temperature and pressure above their critical point are termed as supercritical fluids. They possess high diffusivity and solvolytic efficiency and the density of the fluid can be adjusted by changing the temperature and pressure [207]. In comparison to several supercritical fluids like ammonia, methanol and water, the CO₂ is most widely used and well

recognized supercritical fluid as it has lower critical temperature (31 °C), pressure (73.8 bar), and solubility (7.118 (cal/cm³)^{0.5}) (Table 3) [4, 208]. These properties make it an efficient solvent for different monomeric and non-polar compounds and inefficient for the polymeric and polar compounds. Hence, it is very much suitable to fractionation of LCB as compared to other solvents. CO₂ can easily penetrate the surface of lignocelluloses and reduces recalcitrance and enhances the penetrability of the cellulose [4]. Further, supercritical fluids can be considered as potential option for the pretreatment of LCB because of relatively mild pretreatment conditions, higher fermentable sugar yield, lower inhibitory compound generation, and greater exposure for enzymatic hydrolysis with reduced use of chemicals [209].

A very recent study employing Sc-CO₂ for date pulp pretreatment, reported the temperature and pressure as significant parameters and achieved a maximum sugar yield of 74.1 g/100 g for Sc-CO₂ pretreated date pulp at 10 MPa and 46 °C for 59 min [210]. Zhao et al. (2019) conducted pretreatment of different agricultural residues (corn stover, corn cob, and sorghum stalk) having 75 wt % moisture content using supercritical CO₂, at low temperature (50–80 °C) and a pressure of 17.5–25.0 MPa. After enzymatic hydrolysis of pretreated biomass, a 3 to 4-fold increase in sugar yield was observed as compared to control [211]. In a similar study on blue agave bagasse 40% increase in total reducing sugars was achieved with enzymatic hydrolysis of Sc-CO₂ pretreated biomass [212]. Mitraka et al. (2022) examined the effect of Sc-CO₂ pretreatment on sewage sludge biogas production and observed an increase of 8.7% increase in methane production [213].

Sulfite Pretreatment

The Sulfite Pretreatment to Overcome the Recalcitrance of Lignocellulosics (SPORL) is often abbreviated as SPORL. This method in its first step employs the treatment of biomass with calcium or magnesium sulfite which in turn removes the hemicellulosic and lignin fractions followed by the reduction of size using disk miller [45, 190, 214]. Further new sulfite pretreatment methods have been developed which can utilize various sulfite or bisulfite solutions with broad range of pH and temperatures to weaken the structural components of the LCB (Table 3). This pretreatment method is specially intended and established for the woody biomass, softwoods such as pines and other coniferous plants, hardwood like poplar, willow tree, eucalyptus etc. [215]. This method has high scale up potential for industrial application. The reduced energy requirements for the size reduction and enhanced enzymatic saccharification of pretreated biomass within shorter period of reaction make this method much suitable for the fermentative ethanol production [215]. However, there are still some prone and cons associated with

sulfite pretreatment of LCB, need to be tackled before real time implementation of this method at a commercial scale.

Biological Pretreatment Methods

Biological pretreatments are considered to be nontoxic and eco-friendly in nature, require less energy, and generate no inhibitors; hence, minimize the cost of subsequent downstream processing (though overall cost of biological pretreatment is higher than other pretreatment method). Several bacterial and fungal strains possess the enzymes (ligninases), which can degrade the LCB are being utilized for the biological pretreatment. Among the various lignin degrading microbes, white-rot fungi, especially selective delignifiers, have received much research interest over non-selective delignifiers due to high lignin-free cellulosic biomass yield [1]. Likewise, ligninases possess a critical role in the modification and degradation of lignin biopolymers. The structural rigidity of lignin, mandate the lignolytic microorganisms to produce an array of extracellular oxidative enzymes to achieve efficient degradation. Broadly, these extracellular oxidative machineries include; laccase, manganese peroxidases, lignin peroxidases, and versatile peroxidases that catalyse a direct role in lignin degradation [234]. Additionally, some other ancillary enzymes, such as glyoxal oxidases, feruloyl esterase, alcohol oxidases, aryl-alcohol dehydrogenase, and quinone reductase, which enhance the peroxidase activities and facilitate the lignin fractionation, are being recognized as the sole component of lignin degradation system of microbes [235].

The biological method of pretreatment in general used for the breakdown of cellulose and depolymerization of lignin [11, 236]. The efficiency of the biological pretreatment method highly depends on the temperature, size of biomass, moisture content, incubation time, aeration, accessible surface area, pH, and composition of culture media like source of carbon and nitrogen, cellulose crystallinity, inorganic and organic compounds, roles of enzymes and hydrolysates, microbial strain etc. These factors considerably affect the rate of pretreatment and play vital role in modifying physico-chemical structure of the LCB [237]. Some recent studies on biological pretreatment methods and their effects on further processing are summarized in Table 4.

Zanellati et al. (2021) explored and evaluated the phenol and furan degrading fungi for biological pretreatment of LCB. The study analyzed 40 fungal strains having capability to grow on different concentrations of furfural, vanillin, 4-hydroxybenzaldehyde, and syringaldehyde. *Byssoschlamys nivea* MUT 6321 was found as the only fungus that can grow on all the four molecules present simultaneously [238]. Arora et al. (2016) evaluated the effect of biological pretreatment method for paddy straw. The saccharification efficiency of

white-rot fungus, *Trametes hirsute* treated biomass was evaluated in comparison to steam pretreated biomass. The cellulose content in steam and biological pretreated biomass was found 39.5 and 37.6%, respectively, whereas lignin content was observed 14.2 and 4.7%, respectively. The saccharification efficiency was also found similar for steam as well as biological pretreatment [239]. The conventional pretreatment methods using single microbial culture are economically non-viable as it usually takes longer incubation time. Therefore, to overcome these obstacles mixed microbial consortium or microbial co-cultures should be utilized to increase the lignin degradation efficiency and to reduce pretreatment time.

Conclusions

The lignocellulosic biorefinery is a more sustainable future for human's low value resources. Lignocellulosic biomass and pretreatment strategy represent the crucial factors in attaining these concepts. Selection of cheaper pretreatment process can ensure economical and sustainable viability of a biorefinery process. Furthermore, it becomes mandatory to completely operate the biomass source with minimum loss of mass and waste generation. Physico-chemical and thermo-chemical conversion processes have the potential to meet the technical and economical objectives of a biorefinery framework.

This review article concludes that the eco-friendly pretreatment processes which utilize the green solvents and low chemical loads receiving much interest as compared to the conventional chemical-based pretreatment methods and such methods are being developed and made feasible for industrial application. In recent past deep eutectic solvents have extensively been explored for their feasibility to fractionate variety of LCB. Further selection of pretreatment method highly depends upon type of the biomass to be treated and the purpose or end use for which biomass needs to be pretreated. Following points need to be taken care of while choosing a pretreatment method:

- The pretreatment method employed should considerably be able to alter the complex three dimensional structure of the lignocellulose by depolymerizing its different components and decrystallization of cellulose.
- The method should be able to increase the porosity and surface area of lignocellulose leading to increased enzyme accessibility for hydrolysis of biomass.
- After hydrolysis of pretreated pulp, the total reducing sugar recovery should be close to the theoretical sugar yield.
- The generation of inhibitory compounds and sugar degradation products should be at such minimum level that

- detoxification step prior to hydrolysis or fermentation should not be required.
- Pretreated pulp or liquid processing like washing, separation, neutralization, etc. should be inexpensive and easy to process.
 - Equipments and vessels used for the pretreatment should be simple and capable of processing large quantities of solids with easy operation in terms of commissioning and decommissioning.
 - Pretreatment methods with mild process conditions should be favored.
 - The methods with lesser requirements of chemicals and water should be favored.

Table 4 Comparative analysis of different biological pretreatment methods

Pretreatment method	Biomass	Pretreatment conditions	Key findings	References
White-rot fungus <i>Trametes hirsute</i>	Paddy straw	Incubation Temp.: 30 °C Time: 7 days	Cellulose content: 37.6% Delignification: 71.34%	[239]
White rot fungus <i>Trametes versicolor</i>	Co-digestion of manure with triticale	Incubation Temp.: 25 °C Time: 6 days	Improvement in methane yield by 18% and cellulose degradation by 80% respectively	[240]
White-rot fungus <i>Ceriporiopsis subvermispora</i>	Sugarcane bagasse	Incubation Temp.: 27 °C Time: 60 days	Lignin and xylan losses reached 48% and 47% respectively Glucose recovery: 47%	[241]
White-rot fungus <i>Phlebia brevispora</i>	Corn stover	Incubation Temp.: 28 ⁰ C Time: 42 days Moisture content: 84%	Total sugar yield: 442 mg/g Ethanol yield: 36 g from 150 g pretreated biomass	[242]
White rot fungus <i>Irpex lacteus</i> followed by dilute acid pretreatment	Olive tree biomass	Incubation Temp.: 30 °C Time: 28 days Dilute acid pretreatment: H ₂ SO ₄ conc.: 2% (w/v) Temp.: 130 °C Time: 90 min	Enhancement of enzymatic hydrolysis yield by 34% compared to acid pretreatment alone	[243]
Fungal sp. <i>Galactomyces</i> sp. followed by DES	Bamboo shoot shell	Incubation Temp.: 30 ⁰ C Time: 3 days DES: Choline chloride/oxalic acid ratio: 1:2 (mol/mol) Temp.: 120 °C Time: 1.5 h	Reducing sugar and glucose yields: 81.0% and 74.1% respectively	[244]
Lignolytic Bacterium <i>Bacillus</i> sp.	Rice straw (RS)	Incubation Temp.: 37 °C pH: 7 Time: 7 days	Decrease in lignin content: 53.1% Cumulative maximum biogas production: 528.9 mL/g VS Increase in methane yield: 76.1%	[245]
Mixed microbial culture pretreatment	Corn straw	Temp.: 30 °C Time: 14 days	Degradation rates of hemicellulose, cellulose and lignin: 44.4%, 34.9% and 39.2% respectively Highest daily biogas production: 780 mL Highest methane content: 61.9%	[246]
Microbial consortium	Corn stover	Detoxification bacterium <i>Pseudomonas putida</i> and lactic acid production specialist <i>Bacillus coagulans</i> Temp.: 30 °C Time: 24 h	Degradation rate of organic acids (acetate, levulinic acid) and conversion rate of furan aldehyde: 100% Removal of monoaromatic compounds: 90% Lactic acid yield: 0.8 g/g total sugars	[247]
Bacterium <i>Cupriavidus basilensis</i> followed by dilute acid pretreatment	Rice straw	Incubation Temp.: 30 °C Time: 3 days Dilute acid pretreatment: H ₂ SO ₄ conc.: 0.5% (w/v) Temp.: 121 °C Time: 40 min	Enzymatic digestibility increased by 70% and 244% in bacteria enhanced dilute acid pretreatment compared to only dilute acid pretreatment and untreated rice straw respectively	[248]

- Pretreatment Methods with green and easy to recover chemicals should be favored to avoid further waste processing.
- Pretreatment methods favoring higher extent of fractionation having capability of generating lignin and cellulose rich fraction of high purity should be favored. The purity lignin can further be valorized to variety of high value products.

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