International Journal of Biological Macromolecules 202 (2022) 256–268

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Review

# Development of different pretreatments and related technologies for efficient biomass conversion of lignocellulose

Min Zhou, Xingjun Tian *

*School of Life Sciences, Nanjing University, Nanjing 210023, People's Republic of China*

A R T I C L E I N F O

*Keywords:*
Biomass resource
Lignocellulose
Pretreatment
In situ saccharification
Fermentation
Chemical catalysis

A B S T R A C T

Lignocellulose, a kind of biological resource widely existing in nature, which can be transformed into value-added biochemical products through saccharification, fermentation or chemical catalysis. Pretreatments are the necessary step to increase the accessibility and digestibility of lignocellulose. This paper comprehensively reviewed different pretreatment progress of lignocellulose in recent year, including mechanical/thermal, biological, inorganic solvent, organic solvent and unconventional physical-chemical pretreatments, focusing on quantifying the influence of pretreatments on subsequent biomass conversion. In addition, related pretreatment techniques such as genetic engineering, reactor configurations, downstream process and visualization technology of pretreatment were discussed. Finally, this review presented the challenge of lignocellulose pretreatment in the future.

## 1. Introduction

The development of sustainable energy is very essential to alleviate the problems of energy crisis and environmental pollution [1,2]. Lignocellulosic is a potential resource [3,4], widely exists in the cell wall, can be converted into promising products, including soluble sugars, biofuels, functional materials and fine chemicals [5,6]. As shown in Fig. 1, lignocellulosic wastes, mainly originated from agricultural wastes, forestry wastes, industrial residues, etc.

The value of lignocellulose is mainly related to its three primary components, namely cellulose (35–45%), hemicelluloses (15–30%) and lignin (20–30%) [19–21]. Cellulose and hemicellulose can be converted to reducing sugars after enzymatic hydrolysis, and can be further converted into other chemical products [22,23]. Lignin is a heterogeneous polymer feedstock, can be converted into alkanes through depolymerization and hydrogenation reaction [24,25]. However, the inherent complex polymer structure, highly-ordered hydrogen bonds and the indigestibility of lignin restrict the conversion of lignocellulose [26,27]. Therefore, pretreatment of lignocellulosic biomass in practical operation is necessary and studied extensively [28].

Pretreatment is helpful to improve the biocompatibility, bioconversion yield and enzyme accessibility of lignocellulose [29,30], the benefits of pretreatment were summarized in Fig. 1. Different lignocellulose and pretreatment methods affect the pretreatment effect and subsequent biomass conversion [31,32]. For example, studies have investigated that, the effect of acid-base pretreatment is more obvious on lignocellulose with lower lignin content [11], ionic liquid (IL) pretreatment selectively degraded the G-type lignin fractions compared with the S-type lignin fractions [33]. The current challenges of pretreatment are mainly focused on the mechanism of different types of lignocellulose.

In this review, the characteristics of pretreatment methods include mechanical/thermal, biological, inorganic solvent, organic solvent, unconventional physical-chemical pretreatment methods were summarized, the revealing of pretreatment mechanisms and the quantification of the influence on subsequent biomass conversion were particularly emphasized. Furthermore, other related pretreatment techniques such as genetic engineering, reactor configurations, downstream process, visualization technology of pretreatment were also discussed. Based on the review, we provided a comprehensive perspective for effective pretreatment to improve the biomass conversion capacity.

## 2. Mechanical/thermal pretreatment

### 2.1. Mechanical pretreatment

Mechanical pretreatments include crushing, ball milling, ultrasonic vibration and so on. The main purpose of these methods is to increase the specific surface area (enzyme accessibility) and to improve mass and

---

* Corresponding author.
*E-mail address:* tianxj@nju.edu.cn (X. Tian).

https://doi.org/10.1016/j.ijbiomac.2022.01.036
Received 5 November 2021; Received in revised form 3 January 2022; Accepted 6 January 2022

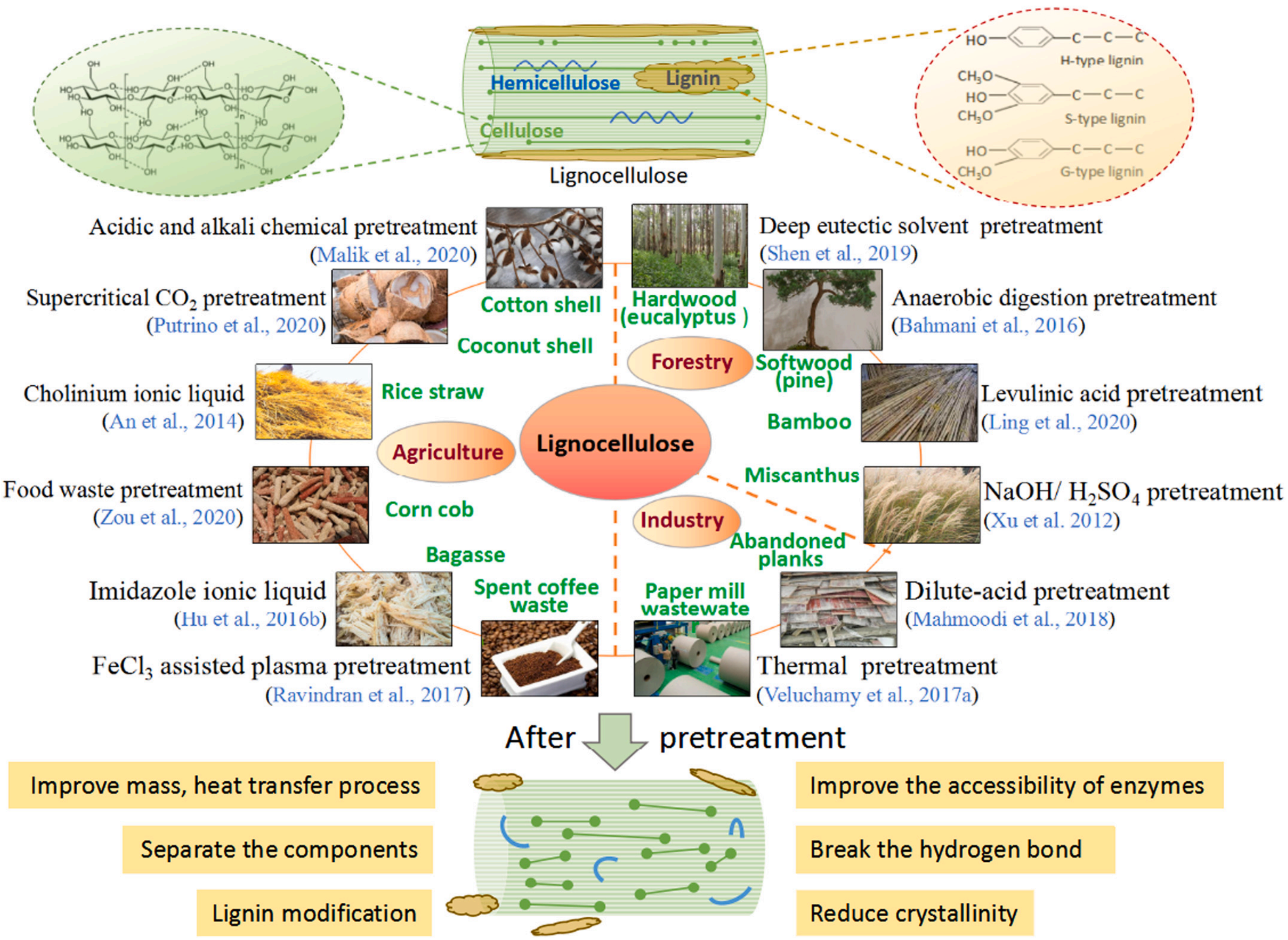

**Fig. 1.** Common types and corresponding pretreatments of lignocellulosic biomass. (Based on and reproduced from [7–18]).

heat transfer [34,35]. The characteristics of the common mechanical pretreatments were summarized in Fig. 2.

Researches supported that the larger size of corn stover were more recalcitrant to hydrolysis than the smaller size of corn stover [36]. The common crush instruments include cutter mill [37], hammer mill [38], variable speed rotor mill [39], etc. Ball milling, a typical mechanical pretreatment, commonly used in promoting non-degradable dissolution and acetylation of lignocellulose [40–42]. Ball milling caused drastic depolymerization of hemicelluloses, which increased the release of monosaccharides in the absence of enzymes [43,44]. Research has demonstrated that the carbohydrate conversion rate of the pretreated maize stem material increased to 79% after 4 h ball milling [44]. Ultrasound is a kind of mechanical wave [45,46], ultrasonic pretreatment reduced the viscosity of the carboxymethyl cellulose solution and decreased the activation energy of the reaction, thereby increasing the value of Vmax of cellulase to 1.3 times than its original value [47].

In addition, wet mechanical pretreatments have the superiority of reducing solvent consumption [48,49], may be a promising new method in biorefining. Glycerol swelling [50], metal salts [51], cosolvents [40], acids [48], etc. have been reported to play a positive role in assisting mechanical pretreatment. Huang et al. proposed a novel pretreatment method using a small amount of dilute alkali (only 4.0% NaOH) to assist ball milling for 60 min, 55.74% of sugars yield was obtained from pennisetum [49].

### 2.2. *Thermal/hydrothermal pretreatment*

Insoluble and acid soluble lignin of lignocellulose increased but hemicellulose content decreased after thermal pretreatment [16,52,53]. Studies showed that, the hemicellulose was significantly converted after pretreatment at 250 °C and 275 °C, the yield of levoglucan was significantly reduced at 300 °C [54,55]. Thermal pretreatment can not only directly affect lignocellulose, but also indirectly affect the conversion of lignocellulose by affecting microorganisms. For example, heat pretreatment increased the availability of acidogenic microorganisms [16,56]. Hydrothermal pretreatment, a kind of pretreatment that employs liquid at high temperature and high pressure [57], has been proved to be an efficient method to release the hemicellulose [58,59]. The maximum yield of furfural up to 21% was obtained after hydrothermal pretreatment (190 °C, 60 min) of corncob [60].

The reaction temperature was the most crucial factor in removal of hemicellulose [61,62]. However, high temperature produced high energy consumption and had inhibitory effect on enzyme activity. These problems need to be further studied and resolved. The thermal/hydrothermal pretreatment needs to be optimized to obtain the maximum enzymatic digestibility and collect heat energy.

### 2.3. *Thermo-mechanical pretreatment*

Steam explosion is a common thermo-mechanical pretreatment that converts the internal energy of steam into mechanical energy (Fig. 3).

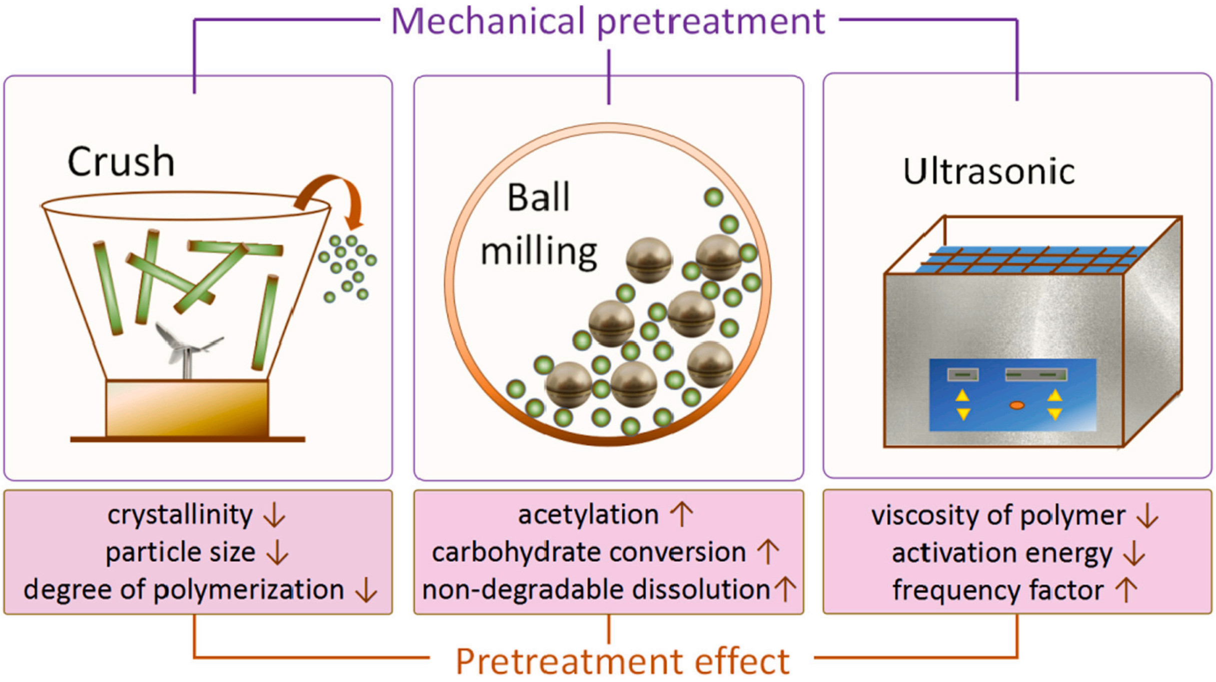

**Fig. 2.** Different mechanical pretreatments and their pretreatment effect.

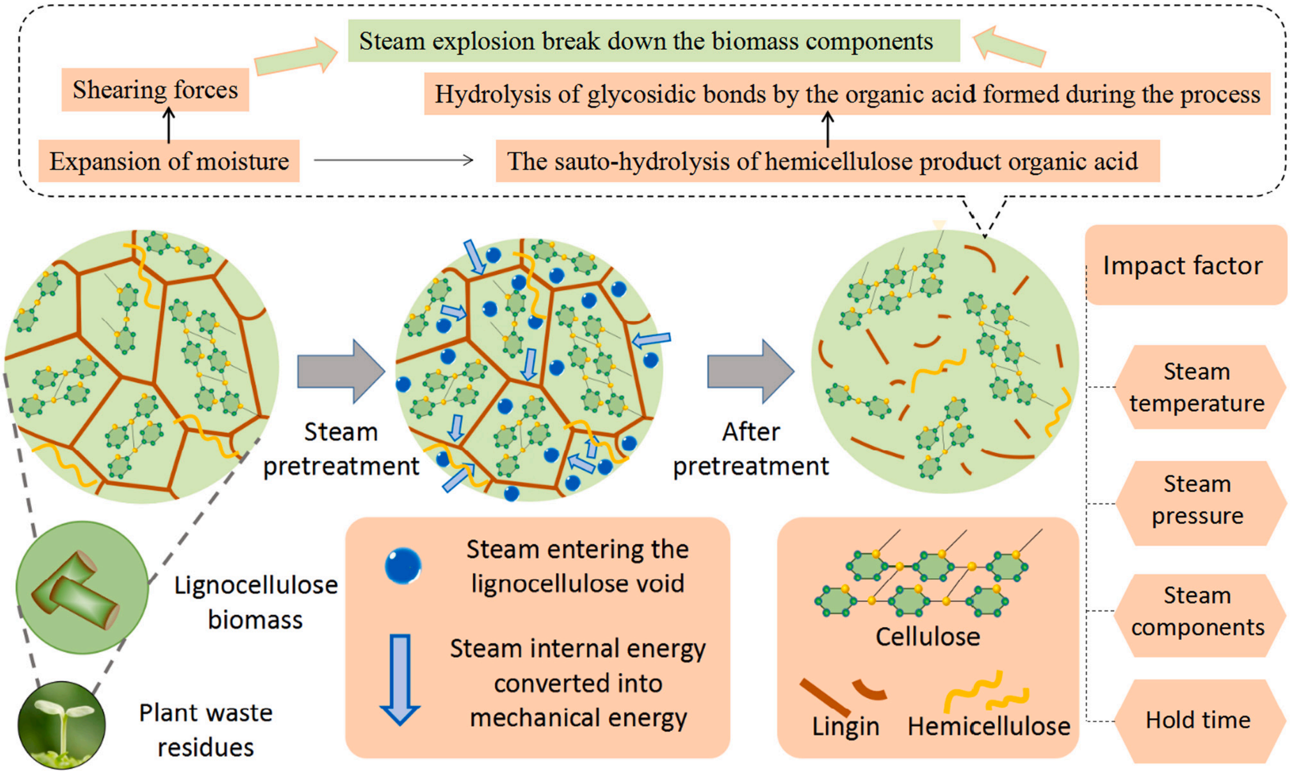

**Fig. 3.** Process and impact factors of steam pretreatment.

Steam explosion pretreatment is the most cost-effective choice for herbaceous and hardwood biomass, but is less effective for softwood because hemicellulose portion of softwood has low content of acetyl groups [63,64]. Moreover, the shearing force generated by the steam explosion makes the hemicellulose glycosidic bonds hydrolyze, thereby generating organic acids [65], the presence of organic acids affect the microbial community. In Miguel's study, cow manure and straw were pretreated by steam pretreatment, 70% ethanol yield was obtained in the best pretreatment conditions (200 °C, 5 min, pH 2) [66].

The steam of the pretreatment can be not only gaseous components (such as $SO_2$ or $CO_2$) [67], but also liquid chemical components (such as acid or alkali) [68,69]. For example, alkali steam explosion is effective for pretreatment of xylan-rich biopolymers. Aspen wood and sugarcane trash were impregnated with NaOH before steam explosion, the highest

**Table 1**
Summary of the impact of different biological pretreatment for lignocellulose biomass.

| Biological pretreatment | Specific pretreatment method | | Lignocellulose type | Biomass conversion | References |
|---|---|---|---|---|---|
| Microbial pretreatment | Fungi | Brown rot fungal (16 weeks, 30 °C) | Aspen, spruce, corn stover (40 mesh) | SY increased by 3 fold | [71] |
| | | *Amorphothecaresinae* ZN1 (24 h, 25 °C) | Corn stover (10% w/v solid loading) | SYD up to 93.2% | [72] |
| | | *Phanerochaete chrysosporium* (30 d, 29 °C) | Rice straw (96.6% w/w solid content) | SYD achieved 64.9% | [73] |
| | Bacteria | *Cupriavidus basilensis* B-8 (2 d, 30 °C) | Rice straw (10% w/v solid loading) | SY increased by 13–31% | [74] |
| | | *Pandoraea* sp. B-6 (2 d, 30 °C) | Air-dried rice straw (10% w/v solid loading) | SY increased by 40.9% | [75] |
| Biological anaerobic digestion pretreatment | Food waste (FW) pretreatment (6 d, 37±1 °C) | | Corn cob (12.5–25 wt%) | MY achieved 401.6 mL/g·VS | [18] |
| | Anaerobic digestion process (27 d, 37 °C) | | Rice straw, sycamore, pine (1% w/v solid loading) | Biofuels increased by 3.6–4.6 fold | [8] |
| | Thermophilic cellulose-degrading microbial (14 d, 50 °C) | | Municipal solid waste (1% w/v solid loading) | MY increased by 2.08 times | [76] |
| | Microaerobic barley straw-adapted microbial (35 d, 25–27 °C) | | barley straw, meadow hay (5% w/v solid loading) | MY increased by 40 times | [77] |
| | Fenton pretreatment + compost (60 d, four temperature phases) | | Rice straw (50–60% moisture) | Suitable microbial environment increased enzyme production | [78] |
| Enzymatic pretreatment | Hemi-cellulose related | Xylanase (72 h, 50 °C) | Wheat straw (3.8% w/w total solids) | Synergism and hydrolysis increased by 29.5% and 10% | [79] |
| | Lignin related | Lignin peroxidase (LiP) | – | Oxidized nonphenolic lignin by generating cation radicals | [80] |
| | | Manganese peroxidase (MnP) | – | Generated $Mn^{3+}$ as a diffusible oxidizer on lignin | [81] |
| | | Laccase (24 h, 50 °C) | Wheat straw (5% w/v total solids) | Glucose and xylose yield increased by 16 and 6% | [82] |

SY, saccharification yield; SYD, saccharification yield digestibility; MY, methane yield.

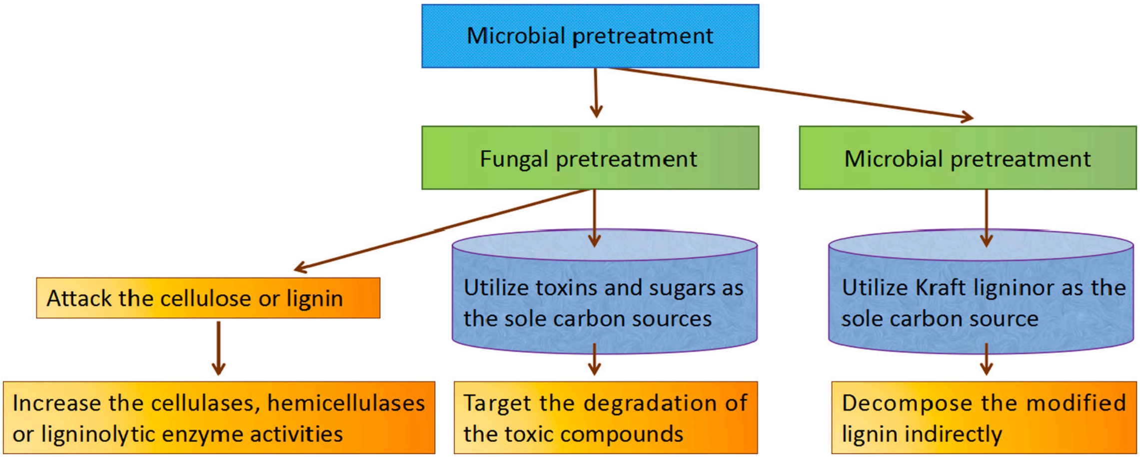

**Fig. 4.** Main principles of microbial pretreatment.

xylan yields of Aspen wood and sugarcane trash achieved 24% and 51%, the maximum cellulose digestibility achieved 81% and 92%, respectively, after pretreatment (204 °C, 10 min) [68]. In addition to steam explosion, there are some other thermo-mechanical pretreatment methods, such as continuous twin screw drive reactor combined with hot water pretreatment [70]. From an environmental and economical point of view, thermo-mechanical reduces the use of additional equipment (washing and filtration systems) and generates less waste water, thereby increasing the concentration of fermentable sugars.

## 3. Biological pretreatment

Biological pretreatments are environmentally friendly process under mild condition. Biological pretreatment methods include microbial pretreatment [50,74], anaerobic digestion pretreatment and enzymatic pretreatment, etc. Table 1 presents the impact of different biological pretreatment for lignocellulose biomass.

### 3.1. Microbial pretreatment

Wood-decay fungi, mainly including brown-rot fungi [73,83] and white-rot fungi [84–86], have the abilities to efficiently depolymerize and modify lignocellulose. The saccharification of corn stover enhanced to three folds after pretreated with fungi *Postia placenta* and *Gloeophyllum trabeum* [71]. There are two main principles of fungal pretreatment shown in Fig. 4. Lignocellulose was attacked by strains, resulting in an increase of cellulases, hemicellulases, ligninolytic enzyme activities [87]. Apart from this, the toxic compounds can be degraded during fungal pretreatment, for example, a kerosene fungus strain, *Amorphotheca resinae* ZN1, isolated by Zhang et al., can efficiently use toxins and sugars as the sole carbon sources during pretreatment of corn stover [88].

Bacteria can not directly decompose lignin, but can use Kraft lignin or (modified lignin) as the carbon source (Fig. 4) [89–91]. Some bacteria and chemical pretreatment have significant complementary effects. For example, the ligninolytic bacterium *Pandoraea* sp. B-6 selectively removed the residual lignin caused by acid pretreatment and the sugar release enhanced by 40.9% [75]. Biological pretreatment can greatly promote the subsequent saccharification or fermentation process of lignocellulose. However, the industrial viability of biological pretreatment was limited due to the relatively long pretreatment time and the large loss of cellulose.

### 3.2. Biological anaerobic digestion pretreatment

The microorganisms used for anaerobic digestion are mainly anaerobic bacteria [92,93], such as thermophilic cellulose-degrading microbial [76] and barley straw-adapted microbial organisms [77]. The methane yield of the co-substrate of barley straw and hay was almost 40 times (15.2 L·kg$^{-1}$ TS) that of the control after pretreated with barley straw-adapted microbial consortium for 35 days [77]. In addition, there are some anaerobic digestion technologies such as food waste pretreatment [7] or Fenton combined compost [78]. Supplementation of food waste increased the activities of microorganisms and enzymes, the higher methane output achieved 401.6 mL/g·VS after anaerobic digestion pretreatment (food waste:corncob = 1:6) [7]. The production of biofuel through anaerobic digestion pretreatment of lignocellulose has great potential [15], however, the efficiency of anaerobic digestion and biogas production are sometimes unsatisfactory due to the incomplete digestion. Increasing the amount of effective microorganisms and enzyme activity in fermentation reaction, reducing the energy input and the production of inhibitory compounds may be the main topic of future researches.

### 3.3. Enzymatic pretreatment

One of the main commercial considerations for value-added production from lignocellulose is the cost and the hydrolytic efficiency of enzyme [85]. Some accessory enzymes, such as hemicellulose degrading enzyme (xylanases) or lignin degrading enzyme (lignin peroxidases and laccases) [82,94,95] can reduce the end-product inhibition and non-productive adsorption of cellulase, thereby providing synergistic effects for enzyme hydrolysis [96]. For example, two hemicellulolytic enzymes (α-L-arabinofuranosidase from *Aspergillus niger* and endoxylanase from *Aspergillus nidulans*) increased the synergy degree by 29.5% [79].

The degradation of lignin is mainly achieved by polyphenol oxidases, lignin peroxidases and laccases [80,85]. Lignin peroxidase and manganese peroxidase could oxidize lignin by generating cation radicals [81]. The laccase-mediator systems-induced increase of lignocellulose conversion was due to the modifications of carboxylic groups in the surface of lignin, the decrease in hydrophobicity caused by carboxylic groups might lower irreversible binding of cellulases to lignin [97]. The glucose and xylose production of wheat straw increased by 16 and 6% after pretreated with a bacterial laccase from *Streptomyces ipomoeae* (SilA) [82]. It is worth noting that, the detoxification effect of laccase was controversial. Javier's research did not support that the production of bioethanol can be improved through detoxification of laccase pretreatment [98].

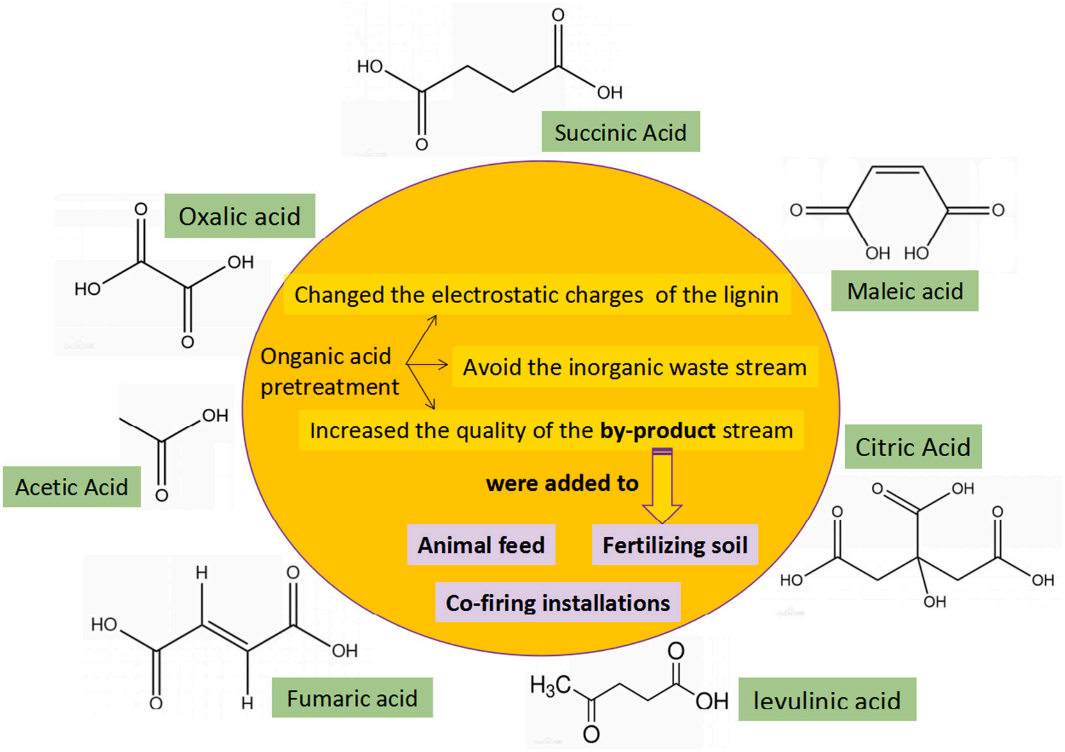

**Fig. 5.** The common organic acid pretreatment solvents and the superiority of organic acid pretreatment methods.

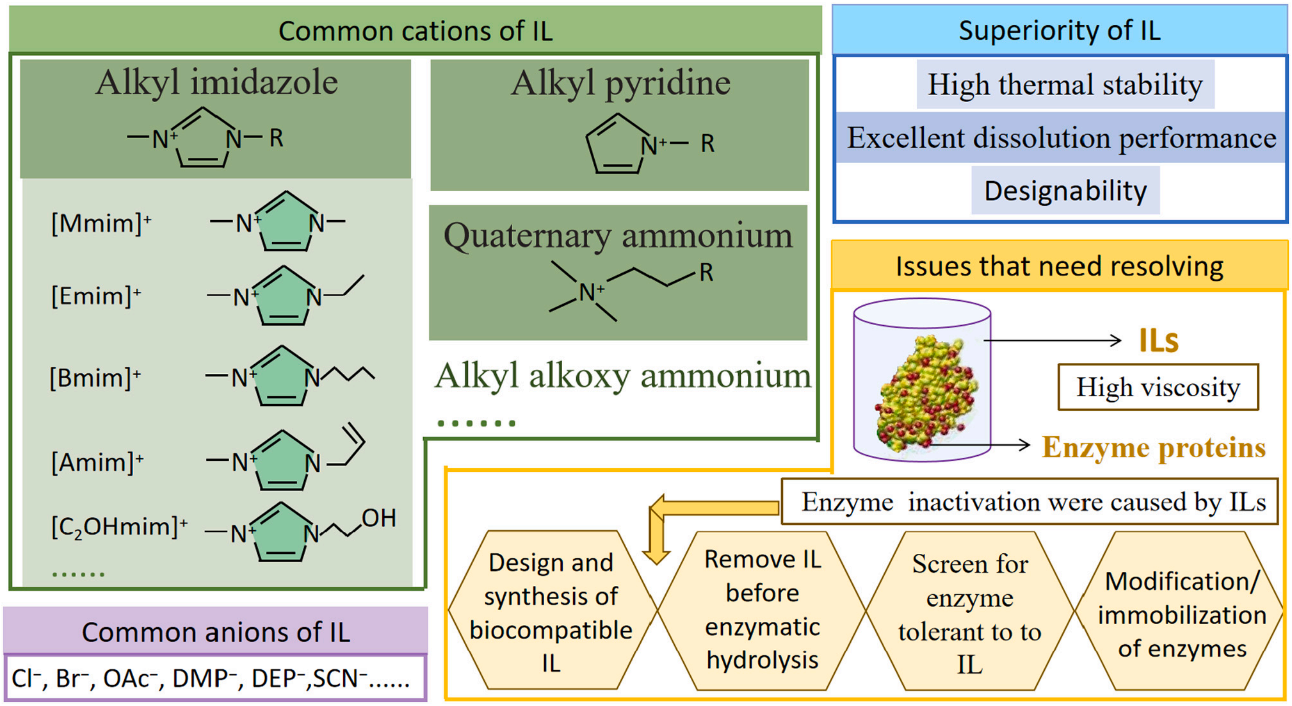

**Fig. 6.** The common cations and anions of ILs, the superiority and issues need to be resolved of IL pretreatment (summarized according to Section 5.2 of this article).

## 4. Inorganic solvent pretreatment

### 4.1. Inorganic alkali/acid pretreatment

Inorganic alkali pretreatment could destroy lignocellulose structure by changing the polymorphous crystal lattice of cellulose and removing part of hemicelluloses and lignin [12,99,100]. It is very effective for the biotransformation of herbaceous biomass, but has limited effects on softwood and hardwood [101,102]. The reducing sugar production of oil palm empty fruit bunch increased after pretreated with even 1% NaOH at 170 °C [103]. Other alkaline reagents such as calcium hydroxide (CaOH) and alkaline $H_2O_2$, etc. were also used in pretreatment [104,105]. After alkali pretreatment, the reducing end groups of cellulose were converted into stable carboxylic groups, the lignin was converted into aromatic monomers contained higher G-rich lignin [106–109].

Inorganic acid mainly include $H_2SO_4$, HCl, $HNO_3$, etc. [110,111]. Inorganic acid pretreatment can not only pretreat hardwood, softwood, agricultural crops, herbaceous residues, but also municipal solid waste [11,112]. Jung et al. used 1% (w/v) dilute sulfuric acid to pretreat oil palm empty fruit bunches at 190 °C for 3 min. The enzyme digestibility of oil palm empty fruit bunches obtained 88.5% of the theoretical glucose production after 48 h of hydrolysis [113]. There are also some innovations in the inorganic acid pretreatment in recent years. For example, a base pH approximation method was proposed by Han et al. to correct fluctuating acid pretreatment efficiency through a simple titration procedure [114].

In summary, the wall polymers were dissociated by extracting crosslinked lignin and hemicelluloses during alkali pretreatment, whereas partial release of lignin monomers and monosaccharides by splitting strong chemical bonds were induced during acid pretreatment [95,115–117]. At present, researches on alkali or acid pretreatment mainly focuses on the pretreatment mechanism and subsequent biomass conversion efficiency. However, the applicability of different lignocelluloses and the formation of inhibitory by-products also need further explore.

### 4.2. Inorganic salt pretreatment

At present, a new method "sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL)" has been developed [118,119]. SPORL produced easily digestible substrates contained few fermentation inhibitors and recovered fermentable sugars from hemicellulose [120,121]. Furthermore, some lignin could dissolved in sulfite waste liquid in the form of lignosulfonate [122]. SPORL process was suitable for hardwood and softwood [118]. Almost completely cellulose conversion to glucose had been achieved after pretreated hardwood with 4% sodium bisulfite at 180 °C for 30 min [123]. SPORL process avoided the corrosion of reactor, without neutralize the substrate before enzymatic hydrolysis. However, there are few studies about other inorganic salt pretreatment in addition to sulfite, the novel inorganic salt pretreatment methods and pretreatment effect needs further verification.

## 5. Organic solvent pretreatment

### 5.1. Organic acid pretreatment

Solvents in organic acid pretreatment include maleic acid, succinic acid , acetic acid, levulinic acid, oxalic acid, etc. [10,124,125]. Fig. 5 demonstrated the common organic acid pretreatment solvents and the superiority of organic acids pretreatment methods. Researches have shown that, organic acid (fumaric, maleic acid) has a greater impact on the conversion of furfural during fermentation compared with inorganic acid (sulfuric) pretreatment at 150 and 170 °C [126]. In addition, a large amount of inorganic waste was generated during inorganic acid pretreatment, but the by-product streams generated by organic acid pretreatments were logically easier to added to animal feed, fertilizing soil and co-firing installations [10]. It is worth noting that in Lan's study, the organic acid (p-toluenesulfonic acid) pretreatment increased the adsorption of cellulase to the substrate by changing the electrostatic charges and hydrophobicity of the biomass components [127]. At present, there are many studies on the synthesis of novel organic acids, the mechanism of organic acids pretreatment and the recycling processes of organic acid are worth exploring.

**Table 2**
Effect of different DES pretreatment methods.

| Ratio of homogeneous mixture of DES (hydrogen bond donor: hydrogen bond acceptor) | Pretreatment condition | Lignocellulose | Biomass conversion | References |
|---|---|---|---|---|
| Lactic acid:ChCl = 10:1 | 110 °C, 6 h | Eucalyptus<br>(10% w/v) | SY reached 94.3%, enhanced 9.8 times | [15] |
| Levulinic acid (LA):acetamide (Am) = 2:1<br>Levulinic acid (LA):betaine (Ba) = 2:1<br>Levulinic acid (LA):ChCl = 2:1 | 120 °C, 2 h | Moso bamboo<br>(1% w/v) | SY achieved 79.07% | [10] |
| Ethylene glycol (EG):ChCl = 2:1 | 130 °C, 30/45 min | Switchgrass<br>(14/20/27% w/v) | SY achieved 86.2% | [145] |
| Glycerol (Gly):ChCl = 2:1<br>Ethylene glycol (EG):ChCl = 2:1<br>Malonic acid (MA):ChCl = 2:1 | 115 °C, 3 h | Rice husk<br>(4% w/v) | SY enhanced 180% | [146] |
| Glycerol (Gly):$K_2CO_3$ = 7:1 | 140 °C, 100 min | Rice straw<br>(1% w/v) | Cellulose content achieved 73.8% | [147] |
| Boric acid (BA):ChCl = 2:5<br>Glycerol (Gly):ChCl = 1:1<br>Glycerol (Gly):betaine = 1:1 | 80 °C, 24 h | Eucalyptus pulp, shredded wheat, etc.<br>(5% w/w) | ED increased from 18% to 33% | [148] |
| Ethylene glycol (EG):ChCl = 1:2<br>Glycerol (Gly):ChCl = 1:2 | 115 °C, 12 h | Rice husk<br>(10% w/v) | SY enhanced 2–3 folds | [149] |
| 4-Hydroxybenzylaldehyde:ChCl = 2:1<br>p-Hydroxybenzoic acid: ChCl = 2:3<br>p-Coumaric acid:ChCl = 1:1 | 100/120/140/160 °C, 1/3/6/9 h | Poplar<br>(10% w/w) | GY and XY achieved 90.8% and 88.9% | [150] |
| p-Coumaric acid:ChCl = 1:1 | 160 °C, 5 h | Herb residues<br>(10% w/v) | ED increased from 48.08% to 84.62% | [151] |

ChCl, choline chloride; SY, saccharification yield; ED, enzymatic digestibility; GY, glucan yield; XY, xylan yield.

### 5.2. Ionic liquid (IL) pretreatment

IL generally composed of an organic cation and a smaller inorganic or organic anion [128–130]. The common cations and anions of IL were summarized in Fig. 6. The IL can be designed and synthesized through changing the anions or cations according to different practical applications [131]. So far, ILs based on alkyl imidazolium cations were the most commonly used IL in lignocellulose pretreatment [132,133]. During imidazolium IL pretreatment, the crystalline cellulose were converted into amorphous structure [134,135], the phenolic hydroxyl groups in lignin were increased [136], resulting in a decrease of molecular weights and achieving the extraction and separation of polysaccharides and lignin [137]. Another common ILs were cholinium ILs [10,138]. The massive removal of lignin and other amorphous components during cholinium IL pretreatment usually led to the neat increase in the biomass crystallinity [139,140].

ILs have the advantages of strong designability and excellent dissolution performance [141]. Nevertheless, the high viscosity of ILs makes them difficult to recycle [142]. Moreover, ILs cause partial or complete inactivation of enzyme proteins [143,144], thereby reducing the efficiency of enzymatic hydrolysis [9]. Thence, as shown in Fig. 6, future researches should focus on designing ILs with different properties to adapt different lignocellulose pretreatment, reducing the viscosity of ILs (such as using co-solvents) and improving the IL tolerance ability of cellulase.

### 5.3. Deep eutectic solvents (DESs) pretreatment

The concept of DESs was firstly proposed by Abbott [152]. DESs are homogeneous mixture composed of a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), its melting point is lower than that of single compound [153,154]. Table 2 listed the ratio of homogeneous mixture of DESs, pretreatment condition and the biomass conversion. The HBD include glycerol (Gly), ethylene glycol (EG), 4-Hydroxybenzylaldehyde and some organic acids, the HBA include acetamide (Am), betaine (Ba), choline chloride (ChCl) and so on.

DES was considered to be one of the most promising and low-cost green pretreatment solvents. The glucose yield by enzymatic hydrolysis was significantly enhanced 9.8 times after DES pretreatment (lactic acid:ChCl = 10:1) compared to the control group [15]. In addition, DES pretreatment showed good recycling performance, lignin could be extracted from La/Ba and EG/ChCl pretreatment liquor [10,145], cellulose could be isolated from $K_2CO_3$-Gly alkaline DES pulping [147]. Most importantly, less influence on the enzyme activity has been verified, the cellulase activity was more than 90% of the original activity in 10% (v/v) Gly based DES and EG based DES [146], xylanase and a variety of cellulases were highly stable in 85% w/w glyceryl-containing DES solvents [148]. However, excellent enzymatic stability in some DESs do not means that it can promote the biomass conversion. The effect and industrial value of DES pretreatment need to be further studied.

### 5.4. Some advanced organic pretreatment solvents

In addition to organic solvents that have been extensively studied such as organic acids, ILs, and DESs, there are other organic solvents provide ideas for future studies on lignocellulose pretreatment, such as γ-valerolactone (GVL), ethylenediamine (EDA), methanol-organosolv, acetone, etc. [155–157]. These novel organic solvents pretreatment even promoted the new concept of preferential lignin biorefinery. For example, the xylose and lignin were solubilized during GVL pretreatment, realized the closed loop biorefining strategy [157]. The break of the ether bonds linking the phenolic monomers of lignin was induced during EDA pretreatment [156]. The lignin content of hazelnut skin was reduced from 39.66% to 34.73% after methanol-organosolv pretreatment [155]. Through acetone pretreatment, 143 g lignin per kg of sweet sorghum bagasse was dissolved into acetone solvent, with the potential to be recovered as unaltered pure lignin [158]. These novel organic solvent pretreatments open up the possibility of selective utilization of lignocellulose biomass especially lignin component [159].

### 5.5. Co-solvents and anti-solvents in pretreatment

The co-solvents used in pretreatment include 1,3-dimethyl-2-imidazolidinone (DMI), *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), DMSO, tetrahydrofuran (THF), etc. [160–164]. Co-solvent reduced the use of organic pretreatment solvent and improved the liquid environment of pretreatment. For example, the viscosity of the ILs/DMSO mixture was lower than that of pure ILs [165,166]. Corncobs residues pretreated with co-solvent THF + $H_2O$ (53.7% THF concentration, 202.3 °C, 1.05 h) had high yield of glucose 498.2 mg/g corncobs residues [164]. The addition of anti-solvent is to separate or remove a

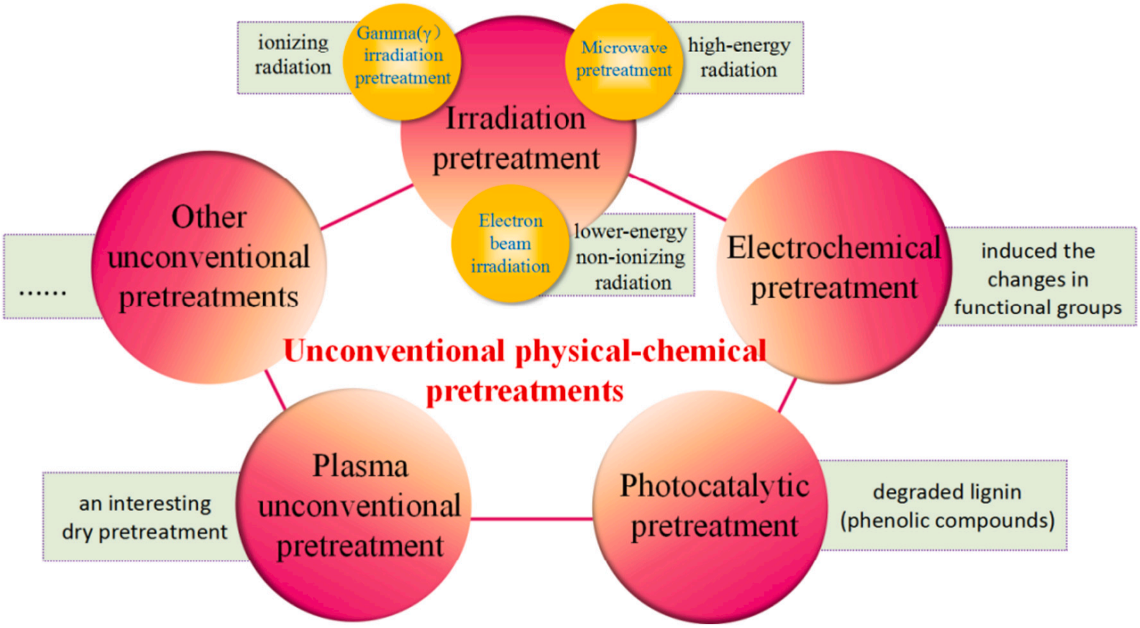

**Fig. 7.** Some unconventional physical-chemical pretreatment methods and their characteristics.

certain component from substances [167]. Alcohols can be used as anti-solvents for pretreatment process. Sathitsuksanoh et al. found that, 1-octanol, as an anti-solvent, caused partial fractionation and multi-phase separation of lignin without damaging the chemical structure of carbohydrates and lignin [168]. In addition, water can also be used as an anti-solvent for lignin or cellulose. Shi et al. provided a better revealing of the duality of water as a co-solvent/anti-solvent to dissolve cellulose [169]. Ideally, co-solvents or anti-solvents synergistic pretreatment should be aimed to reduce cost and increase the efficiency of subsequent enzymatic saccharification and fermentation.

## 6. Unconventional physical-chemical pretreatments

Unconventional physical-chemical pretreatment methods use irradiation/electricity/optical energy and other renewable energy, which may be considered as potential alternatives to traditional pretreatments in the future. Some novel physical-chemical pretreatments irradiation pretreatment, electrochemical pretreatment, photocatalytic pretreatment, plasma unconventional pretreatment, etc. (Fig. 7) have been developed [170].

Irradiation pretreatments mainly include microwave pretreatment, γ irradiation pretreatment and electron beam irradiation pretreatment. The superiorities of Irradiation pretreatment were as follows: reduce the reaction time remarkably and lessen the reaction activation energy [171–174]. Apart from these, the appropriate irradiation dose (891 kGy) could eliminate the negative effect of toxic derived compounds on ethanol bioconversion [171]. The highest ethanol bioconversion (70%) and glucose yield (99.7%) were achieved after adapted the combined proposal of $NaBH_4$ detoxification with irradiation pretreatment [175]. Electrochemical pretreatment induced the disintegration of aliphatic, unsaturated and carbonyl carbon functional groups in biomass [176,177]. The methane production of paper sludge increased by 9.85% after electrohydrolysis pretreatment [178]. Photocatalytic pretreatment could degraded phenolic compounds (lignin) [179], $TiO_2$ photocatalytic pretreatment shorten the time of saccharification and fermentation reaction [180].

Recently, unconventional plasma pretreatment has been developed into an interesting dry pretreatment method [181], highly reactive ionized gas did not produce toxic by-products and pollution [14,182]. On the long run, these unconventional physical-chemical pretreatments may be considered as potential alternatives to traditional pretreatments, especially during periods when renewable energy are relatively easy to obtain.

## 7. Pretreatment related technologies

### 7.1. *Pretreatment and genetic modification technology*

Genetic engineering plays an important role in pretreatment. Firstly, genetic engineering can be regarded as a special biomass pretreatment process, for example, the genetic engineering can change the characteristics of biomass such as molecular polymerization and lignin content of biomass, thereby reduce lignocellulose recalcitrance and increase saccharification production [95,183]. Besides, genetic modification may increase the response of lignocellulose to other pretreatments. For example, there is no significant correlation between lignin content and saccharification efficiency for transgenic biomass without pretreatment, however, the total enzymatic glucan digestibility of transgenic samples (low lignin) was increased to 70% after pretreatment with dilute acid [184]. These conclusions indicated that genetically modified biomass was more sensitive to certain pretreatments. At present, researches on the key genes that determine the enzymatic digestibility and characteristics of lignocellulose are not sufficient enough.

### 7.2. *Pretreatment reactor configurations*

Current biomass pretreatment reactors mainly include batch reactors [185] and flow-through reactors [186]. Flow-through reactors were generally considered to be a more ideal pretreatment strategy than batch reactors [187]. Flow-through reactors consists of feeders, continuous reactors, unloaders, cooling water condensers and receiving tanks [188,189]. Currently, flow-through reactors have been used in different types of biomass pretreatment processes, such as hydrothermal pretreatment [190] thermo-mechanical pretreatment [191], inorganic solvent pretreatment [192], organic solvent pretreatment [193,194].

Compared with batch reactors, the degradation or condensation time of the dissolved carbohydrates and lignin after pretreatment using flow-through reactors were shorter, the redeposition of dissolved lignin rarely occurred, since the slurry was continuously discharged from the reactors [195,196]. In addition, the flow-through reactor had a higher lignin

**Table 3**
Comparison of the characteristics of different pretreatment types.

| Effect of pretreatment | Thermal/mechanical pretreatment | Biological pretreatment | Inorganic solvent pretreatment | Organic solvent pretreatment | Unconventional physical-chemical pretreatment |
|---|---|---|---|---|---|
| Increase substrate accessibility | ✓ | ✓ | ✓ | ✓ | ✓ |
| Less by-products produced | ✓ | ✓ | × | × | ✓ |
| Short pretreatment cycle | ✓ | × | ✓ | ✓ | ✓/× |
| Recyclability | × | × | ✓ | ✓ | × |
| Solvent designability | – | – | × | ✓ | – |
| Remove lignin | ✓/× | × | ✓ | ✓ | ✓/× |
| Modify lignin | × | ✓/× | ✓/× | ✓ | ✓ |
| Mild reaction conditions | ✓/× | ✓ | × | × | ✓/× |

"✓" = match the condition, "×" = not match the condition, "✓/×" = not determined.

removal (up to 70% removal) and a lower inhibitor output than batch reactor, thereby improving the accessibility of cellulose and increasing the substrate digestibility [197]. For example, a pilot-scale continuous tubular reactor was used in glucose fermentation and sequential saccharification, the highest sugar conversion of agave bagasse, wheat straw, corn stover and sugarcane bagasse (4% *w/v* solid loading) were 83.3% , 82.8% , 76.1% and 51.8%, respectively [198]. For another example, sulfuric acid-assisted (4.0–5.5 wt% $H_2SO_4$)) continuous twin screw-driven reactor (CTSR) pretreatment were used in ethanol production, the cellulose content of poplar sawdust was increased by 74.9–76.9%, the highest enzymatic hydrolysis digestibility was 73.6% [199].

At present, the commercialization of biomass pretreatment reactors has the challenge of durability and stability. The final product concentration is relatively low due to the consumption of a large amount of hot water, so the process conditions of flow-through reactors need to be further improved [186]. Some related reactor technologies such as screw conveyor reactors and fixed bed reactors [187] need to be studied in more detail. In addition, the kinetic model of the pretreatment reactors needs further verification and development.

### 7.3. *Downstream process after pretreatment*

As we all know, lignocellulose converted to smaller products or intermediate products, such as bio-oil, glucose, xylose, HMF, furfural, phenolic monomers or dimers after pretreatment [27]. There are many tradeoffs in the downstream process after pretreatment, which need to have an economically considerations [32,200]. For example, in Kumar's study, the production cost based on the feedstock and enzymes were calculated after dilute alkali, steam explosion, dilute acid and hot water pretreatments, each liter of ethanol production required $0.88, $0.85, $0.83, and $0.81 after different pretreatment, respectively [201]. Recently, one-pot technologies such as simultaneous saccharification and co-fermentation were considered as economical process. However, some pretreatment solvents may cause partial inactivation of enzymes [9]. Studies have shown that the modification or immobilization of enzymes were beneficial to increase enzyme activity and recyclability [202], and improve the downstream production efficiency of one-pot pretreatment. In addition, a variety of additives, such as metal ions, hydrophilic polymers, surfactants, can alter the microenvironment of pretreatment, thereby improving the stability of enzymes [203–205]. For example, the addition of non-ionic surfactant Tween 20 changed the surface charges, hydrogen bonding ability and hydrophobicity of cellulase, reduced the non-productive adsorption of enzyme proteins [206].

Pretreatment is of primary importance for the development sustainable biorefinery process. In addition to economic feasibility, the limitations of each pretreatment on the downstream process were also necessary to consider. Therefore, future researches should focus on improving the downstream process to improve biomass conversion efficiency.

### 7.4. *Visualization technology in pretreatment*

Visualization technology can realize in-depth exploration of the mechanism of pretreatment and enzymatic hydrolysis [207,208]. Visualization analysis equipment include Raman microspectroscopy, confocal laser scanning microscopy (CLSM), Atomic Force Microscope (AFM), etc. [209–211]. For example, Li et al. proposed an approach of label-free Raman microspectroscopy combined with integrating fully constrained least-squares (FCLS) for qualitative, quantitative, and location analysis of the changes in the subcellular lignocellulose after alkali pretreatment [211]. Dong et al. used fluorescent labeling combined with a CLSM, proved that the efficient delignification during pretreatment significantly reduced the non-productive binding of cellulase to lignin [210]. Furthermore, CLSM, AFM, stimulated Raman scattering (SRS) microscopy and bright-field light microscopy were used to better understand the effect of pretreatment on cell wall structure and the process of enzymatic digestion [209]. Visualization analysis technologies combined with the optical amplification capability and the chemical specificity of vibrational spectroscopy, are helpful to further explore the influence of pretreatment and subsequent enzymatic hydrolysis. These technologies have great potential application value in future pretreatment researches.

## 8. Summary and perspective

Pretreatment of lignocellulosic biomass is a prerequisite of biomass conversion. The characteristics of different pretreatment methods were summarized in Table 3 according to this paper. For example, biological pretreatments are environmentally friendly process under mild condition but need a long pretreatment time (weeks to months). Organic solvent pretreatment produced inhibitory by-products, but it have the advantages of solvent designability and recycling. At present, researches on pretreatment mechanism and the influence of pretreatment microenvironment on the catalytic reaction were still insufficient. Future works should focus on the following issues: (I) Design the optimal pretreatment method according to different practical applications. (II) Study the effect of inhibitory by-products product on enzyme proteins and develop pretreatment methods that can reduce by-products. (III) Some unconventional methods and novel technologies (genetic engineering, reactor configurations, downstream process techniques, visualization techniques, etc.) should be more widely used and developed in the analysis of pretreatment, enzyme adsorption and hydrolysis digestion processes.

## Acknowledgements

The authors are grateful for the financial support from The National Natural Science Foundation of China (31870598), The National Key

Research and Development Program of the Ministry of Science and Technology of China (No. 2016YFD0600204), The State Key Program of National Natural Science Foundation of China (No. 3153007), Strategic Priority Research Program of the Chinese Academy of Sciences (A) (XDA19050400).

## References

[1] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, Nature 488 (2012) 294–303.

[2] S. Chu, Y. Cui, N. Liu, The path towards sustainable energy, Nat. Mater. 16 (2017) 16–22.

[3] D. Carpenter, T.L. Westover, S. Czernika, W. Jablonskia, Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors, Green Chem. 16 (2013).

[4] S.H. Mood, A.H. Golfeshan, M. Tabatabaei, G.S. Jouzani, G.H. Najafi, M. Gholami, et al., Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment, Renew. Sust. Energ. Rev. 27 (2013) 77–93.

[5] V. Menon, M. Rao, Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept, Prog. Energy Combust. Sci. 38 (2012) 522–550.

[6] S. Wang, G. Dai, H. Yang, Z. Luo, Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review, Prog. Energy Combust. Sci. 62 (2017) 33–86.

[7] Y. An, N. Li, M. Zong, W. Lou, Easily measurable pH as an indicator of the effectiveness of the aqueous cholinium ionic liquid-based pretreatment of lignocellulose, RSC Adv. 4 (2014) 55635.

[8] M.A. Bahmani, M. Shafiei, K. Karimi, Anaerobic digestion as a pretreatment to enhance ethanol yield from lignocelluloses, Process Biochem. 9 (2016) 1256–1263.

[9] D. Hu, L. Xiao, L. Li, C. Zhong, X. Ju, L. Yan, et al., Effects of ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate on cellulase produced by *Paenibacillus* sp. LLZ1, ACS Sustain. Chem. Eng. 4 (2016) 4922–4926.

[10] Z. Ling, Z. Guo, C. Huang, L. Yao, F. Xu, Deconstruction of oriented crystalline cellulose by novel levulinic acid based deep eutectic solvents pretreatment for improved enzymatic accessibility, Bioresour. Technol. 305 (2020) 123025.

[11] P. Mahmoodi, K. Karimi, M.J. Taherzadeh, Efficient conversion of municipal solid waste to biofuel by simultaneous dilute-acid hydrolysis of starch and pretreatment of lignocelluloses, Energy Convers. Manag. 166 (2018) 569–578.

[12] K. Malik, E. Salama, T.H. Kim, Xi Li, Enhanced ethanol production by Saccharomyces cerevisiae fermentation post acidic and alkali chemical pretreatments of cotton stalk lignocellulose, Int. Biodeterior. Biodegradation 147 (2020) 104869.

[13] F.M. Putrino, M. Tedesco, R.B. Bodini, A.L. Oliveira, Study of supercritical carbon dioxide pretreatment processes on green coconut fiber to enhance enzymatic hydrolysis of cellulose, Bioresour. Technol. 309 (2020) 123387.

[14] R. Ravindran, C. Sarangapani, S. Jaiswal, P.J. Cullen, A.K. Jaiswal, Ferric chloride assisted plasma pretreatment of lignocellulose, Bioresour. Technol. 243 (2017) 327–334.

[15] X. Shen, J. Wen, Q. Mei, X. Chen, D. Sun, T. Yuan, et al., Facile fractionation of lignocelluloses by biomass derived deep eutectic solvent (DES) pretreatment for cellulose enzymatic hydrolysis and lignin valorization, Green Chem. 21 (2019) 275–283.

[16] C. Veluchamy, A.S. Kalamdhad, Enhancement of hydrolysis of lignocellulose waste pulp and paper mill sludge through different heating processes on thermal pretreatment, J. Clean. Prod. 168 (2017) 219–226.

[17] N. Xu, W. Zhang, S. Ren, F. Liu, C. Zhao, H. Liao, et al., Hemicelluloses negatively affect lignocellulose crystallinity for high biomass digestibility under NaOH and $H_2SO_4$ pretreatments in Miscanthus, Biotechnol. Biofuels 5 (2012) 58–69.

[18] H. Zou, Q. Jiang, R. Zhu, Y. Chen, T. Sun, M. Li, et al., Enhanced hydrolysis of lignocellulose in corn cob by using food waste pretreatment to improve anaerobic digestion performance, J. Environ. Manag. 154 (2020) 109830.

[19] K. Chen, J. Sang, Z. Wang, U. Ibrahim, W. Xia, A. Guo, et al., Production of low-oxygenated bio-fuels (hydrocarbons and polymethylphenols) from lignocellulose by a two-stage strategy with non-noble metal catalysts, Fuel 286 (2021) 119401.

[20] T. Mori, Y. Tsuboi, N. Ishida, N. Nishikubo, T. Demura, J. Kikuchi, Multidimensional high-resolution magic angle spinning and solution-state NMR characterization of $^{13}$C-labeled plant metabolites and lignocellulose, Sci. Rep. 5 (2015) 11848.

[21] M. Si, M. Sillanpää, S. Zhuo, J. Zhang, M. Liu, S. Wang, et al., Phase separation of co-solvent promotes multiple bio-nanomaterials conversion from natural lignocellulose, Ind. Crop. Prod. 152 (2020) 112469.

[22] F. Collard, J. Blin, A review on pyrolysis of biomass constituents: mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, Renew. Sust. Energ. Rev. 38 (2014) 594–608.

[23] C.R.M. Monteiro, P.F. Avila, M.A.F. Pereira, G.N. Pereira, S.E. Bordignon, E. Zanella, et al., Hydrothermal treatment on depolymerization of hemicellulose of mango seed shell for the production of xylooligosaccharides, Carbohydr. Polym. 253 (2021) 117274.

[24] E.R. Aguado, A.I. Molina, D.B. Plata, J.A. Cecilia, I.B. Martín, E.R. Castellón, Ni and Fe mixed phosphides catalysts for O-removal of a bio-oil model molecule from lignocellulosic biomass, Mol. Catal. 437 (2017) 130–139.

[25] X. Zhang, Q. Zhang, T. Wang, B. Li, Y. Xu, L. Ma, Efficient upgrading process for production of low quality fuel from bio-oil, Fuel 179 (2016) 312–321.

[26] L. Auer, A. Lazuka, D.S. Dussès, E. Miambi, M. Donohue, G.H. Raquet, Uncovering the potential of termite gut microbiome for lignocellulose bioconversion in anaerobic batch bioreactors, Front. Microbiol. 8 (2017) 2623.

[27] C. Wang, X. Zhang, Q. Liu, Q. Zhang, L. Chen, L. Ma, A review of conversion of lignocellulose biomass to liquid transport fuels by integrated refining strategies, Fuel Process. Technol. 208 (2020) 106485.

[28] M.G. Resch, B.S. Donohoe, P.N. Ciesielski, J.E. Nill, L. Magnusson, M.E. Himmel, et al., Clean fractionation pretreatment reduces enzyme loadings for biomass saccharification and reveals the mechanism of free and cellulosomal enzyme synergy, ACS Sustain. Chem. Eng. 2 (2014) 1377–1387.

[29] J. Hu, Q. Wang, W. Wang, Z. Xu, J. Fu, Q. Xu, et al., Synthesis of a stable solid acid catalyst from chloromethyl polystyrene through a simple sulfonation for pretreatment of lignocellulose in aqueous solution, Chemsuschem 14 (2020).

[30] R. Wahlstrom, J. Rahikainen, K. Kruus, A. Suurnakki, Cellulose hydrolysis and binding with Trichoderma reesei Cel5A and Cel7A and their core domains in ionic liquid solutions, Biotechnol. Bioeng. 111 (2014) 726–733.

[31] K. Karimi, M.J. Taherzadeh, A critical review of analytical methods in pretreatment of lignocelluloses: composition, imaging, and crystallinity, Bioresour. Technol. 200 (2016) 1008–1018.

[32] H. Mahmood, M. Moniruzzaman, T. Iqbal, M.J. Khan, Recent advances in the pretreatment of lignocellulosic biomass for biofuels and value-added products, Curr. Opin. Green Sustain. Chem. 20 (2019) 18–24.

[33] Y. Shao, Q. Xia, L. Dong, X. Liu, X. Han, S.F. Parker, et al., Selective production of arenes via direct lignin upgrading over a niobium-based catalyst, Nat. Commun. 8 (2016) 16104.

[34] C.V.J. Bernardo, B.S. Dien, K.C. Ting, V. Singh, Influence of feedstock particle size on lignocellulose conversion—a review, Appl. Biochem. Biotechnol. 164 (2011) 1405–1421.

[35] S.O. Dahunsi, Mechanical pretreatment of lignocelluloses for enhanced biogas production: methane yield prediction from biomass structural components, Bioresour. Technol. 280 (2019) 18–26.

[36] S.P.S. Chundawat, B. Venkatesh, B.E. Dale, Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility, Biotechnol. Bioeng. 96 (2007).

[37] N. Nasirpour, S.M. Mousavi, Effect of particle size in polyethyltene glycol-assisted [BMIM][Cl] pretreatment of sugarcane bagasse, BioEnergy Res. 14 (2021) 1136–1146.

[38] O.A. Rojas-Rejon, A. Sanchez, The impact of particle size and initial solid loading on thermochemical pretreatment of wheat straw for improving sugar recovery, Bioprocess Biosyst. Eng. 37 (2014) 1427–1436.

[39] J.A. Souza-Corrêa, C. Oliveira, V.M. Nascimento, L.D. Wolf, E.O. Gómez, G.J. M. Rocha, J. Amorim, Atmospheric pressure plasma pretreatment of sugarcane bagasse: the influence of biomass particle size in the ozonation process, Appl. Biochem. Biotechnol. 172 (2014) 1663.

[40] M.H. Sipponen, S. Laakso, S. Baumberger, Impact of ball milling on maize (Zea mays L.) stem structural components and on enzymatic hydrolysis of carbohydrates, Ind. Crop. Prod. 61 (2014) 130–136.

[41] S.V. Vyver, L. Peng, J. Geboers, H. Schepers, F. Clippel, C.J. Gommes, et al., Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose, Green Chem. 12 (2010) 1560–1563.

[42] Y. Wu, S. Ge, C. Xia, C. Mei, K.H. Kim, L. Cai, et al., Application of intermittent ball milling to enzymatic hydrolysis for efficient conversion of lignocellulosic biomass into glucose, Renew. Sust. Energ. Rev. 136 (2021) 110442.

[43] H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita, Fukuoka, high-yielding one-pot synthesis of glucose from cellulose using simple activated carbons and trace hydrochloric acid, ACS Catal. 3 (2013) 581–587.

[44] F. Lu, J. Ralph, Non-degradative dissolution and acetylation of ball milled plant cell walls: high-resolution solution-state NMR, Plant J. 35 (2003) 535–544.

[45] P. Alvira, E.T. Pejó, M. Ballesteros, M.J. Negro, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review, Bioresour. Technol. 101 (2010) 4851–4861.

[46] A.Z. Sulaiman, A. Ajit, Ultrasound mediated enzymatic hydrolysis of cellulose and carboxymethyl cellulose, Biotechnol. Prog. 29 (2013) 1448–1457.

[47] R. Nakayama, M. Murakami, N. Namiki, M. Imai, Impact of ultrasonic irradiation pretreatment of water-soluble cellulose on enzymatic hydrolysis, SN Appl. Sci. 2 (2020) 846.

[48] F. Boissou, N. Sayoud, K.D.O. Vigier, A. Barakat, S. Marinkovic, B. Estrine, et al., Acid-assisted ball milling of cellulose as an efficient pretreatment process for the production of butyl glycosides, ChemSusChem 8 (2015) 3263–3269.

[49] J. Huang, Y. Zhu, T. Liu, S. Sun, J. Ren, A. Wu, et al., A novel wet-mechanochemical pretreatment for the efficient enzymatic saccharification of lignocelluloses: small dosage dilute alkali assisted ball milling, Energy Convers. Manag. 194 (2019) 46–54.

[50] Y. Zhang, M. Huang, J. Su, H. Hu, M. Yang, Z. Huang, et al., Overcoming biomass recalcitrance by synergistic pretreatment of mechanical activation and metal salt for enhancing enzymatic conversion of lignocellulose, Biotechnol. Biofuels 12 (2019).

[51] L. Zhang, H. Lu, J. Yu, Z. Wang, Y. Fan, X. Zhou, Dissolution of lignocelluloses with high lignin content in a NMMO/$H_2O$ solvent system via a simple glycerol swelling and mechanical pretreatment, J. Agric. Food Chem. 65 (2017) 9587–9594.

[52] D. Liu, P. Ning, G. Qu, X. Huang, Y. Liu, J. Zhang, The effects of cathodic micro-voltage combined with hydrothermal pretreatment on methane fermentation of lignocellulose substrate, IOP Conf. Ser Earth Environ. Sci. 64 (2017), 012083.

[53] T. Rogalinski, T. Ingram, G. Brunner, Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures, J. Supercrit. Fluids 47 (2008) 54–63.

[54] M.T. Ashraf, J.E. Schmidt, Process simulation and economic assessment of hydrothermal pretreatment and enzymatic hydrolysis of multi-feedstock lignocellulose — separate vs combined processing, Bioresour. Technol. 249 (2017) 835–843.

[55] F. Nsaful, F.X. Collard, J.F. Görgens, Influence of lignocellulose thermal pretreatment on the composition of condensable products obtained from char devolatilization by means of thermogravimetric analysis–thermal desorption/gas chromatography–mass spectrometry, J. Anal. Appl. Pyrolysis 127 (2017) 99–108.

[56] N. Zhu, J. Gao, D. Liang, Y. Zhu, B. Li, H. Jin, Thermal pretreatment enhances the degradation and humification of lignocellulose by stimulating thermophilic bacteria during dairy manure composting, Bioresour. Technol. 319 (2021) 124149.

[57] G. Yu, S. Yano, H. Inoue, S. Inoue, T. Endo, S. Sawayama, Pretreatment of rice straw by a hot-compressed water process for enzymatic hydrolysis, Appl. Biochem. Biotechnol. 160 (2010) 539–551.

[58] F. Monlau, A. Barakat, J.P. Steyer, H. Carrere, Comparison of seven types of thermo-chemical pretreatments on the structural features and anaerobic digestion of sunflower stalks, Bioresour. Technol. 120 (2012) 241–247.

[59] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, et al., Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresour. Technol. 96 (2005) 673–686.

[60] A. Deng, J. Ren, H. Li, F. Peng, R. Sun, Corncob lignocellulose for the production of furfural by hydrothermal pretreatment and heterogeneous catalytic process, RSC Adv. 5 (2015) 60264–60272.

[61] K. Xu, Z. Shi, J. Lyu, Q. Zhang, T. Zhong, G. Du, et al., Effects of hydrothermal pretreatment on nano-mechanical property of switchgrass cell wall and on energy consumption of isolated lignin-coated cellulose nanofibrils by mechanical grinding, Indust. Crops Prod. 149 (2020) 112317.

[62] J. Zhao, D. Tian, J. Hu, F. Shen, Y. Zeng, G. Yang, et al., Evaluation of hydrothermal pretreatment on lignocellulose-based waste furniture boards for enzymatic hydrolysis, Appl. Biochem. Biotechnol. 192 (2020) 415–431.

[63] M.A. Kabel, G. Bos, J. Zeevalking, A.G.J. Voragen, H.A. Schols, Effect of pretreatment severity on xylan solubility and enzymatic breakdown of the remaining cellulose from wheat straw, Bioresour. Technol. 98 (2007) 2034–2042.

[64] K.H. Kim, J. Hong, Supercritical $CO_2$ pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis, Bioresour. Technol. 77 (2001) 139–144.

[65] A.D. Moreno, D. Ibarra, I. Ballesteros, J.L. Fernández, M. Ballesteros, Ethanol from laccase-detoxified lignocellulose by the thermotolerant yeast Kluyveromyces marxianus—effects of steam pretreatment conditions, process configurations and substrate loadings, Biochem. Eng. J. 79 (2013) 94–103.

[66] M.S. Sebastiá, B. Erdei, K. Kovacs, M. Galbe, O. Wallberg, Introducing low-quality feedstocks in bioethanol production: efficient conversion of the lignocellulose fraction of animal bedding through steam pretreatment, Biotechnol. Biofuels 12 (2019) 215.

[67] V.F. Leitão, C.C. Perrone, J. Rodrigues, A.P.M. Franke, S. Macrelli, G. Zacch, An approach to the utilisation of $CO_2$ as impregnating agent in steam pretreatment of sugar cane bagasse and leaves for ethanol production, Biotechnol. Biofuels 3 (2010) 7.

[68] G.T. Mihiretu, A.F. Chimphango, J.F. Görgens, Steam explosion pre-treatment of alkali-impregnated lignocelluloses for hemicelluloses extraction and improved digestibility, Bioresour. Technol. 294 (2019) 122121.

[69] F. Nielsen, M. Galbe, G. Zacchi, O. Wallberg, The effect of mixed agricultural feedstocks on steam pretreatment, enzymatic hydrolysis, and cofermentation in the lignocellulose-to-ethanol process, Biomass Convers. Bioref. 10 (2020) 253–266.

[70] B.H. Um, C.H. Choi, K.K. Oh, Chemicals effect on the enzymatic digestibility of rape straw over the thermo-mechanical pretreatment using a continuous twin screw-driven reactor (CTSR), Bioresour. Technol. 130 (2013) 38–44.

[71] J.S. Schilling, J. Ai, R.A. Blanchette, S.M. Duncan, T.R. Filley, U.W. Tschirner, Lignocellulose modifications by brown rot fungi and their effects, as pretreatments, on cellulolysis, Bioresour. Technol. 116 (2012) 147–154.

[72] Y.H. Jung, H.K. Kim, H.M. Park, Y. Park, K. Park, J. Seo, et al., Mimicking the Fenton reaction-induced wood decay by fungi for pretreatment of lignocellulose, Bioresour. Technol. 179 (2015) 467–472.

[73] J.S. Bak, J.K. Ko, I. Choi, Y. Park, J. Seo, K.H. Kim, Fungal pretreatment of lignocellulose by *Phanerochaete chrysosporium* to produce ethanol from rice straw, Biotechnol. Bioeng. 104 (2009) 471–482.

[74] Z. Shen, K. Zhang, M. Si, M. Liu, S. Zhuo, D. Liu, et al., Synergy of lignocelluloses pretreatment by sodium carbonate and bacterium to enhance enzymatic hydrolysis of rice straw, Bioresour. Technol. 249 (2018) 154–160.

[75] M. Si, D. Liu, M. Liu, X. Yan, C. Gao, L. Chai, et al., Complementary effect of combined bacterial-chemical pretreatment to promote enzymatic digestibility of lignocellulose biomass, Bioresour. Technol. 272 (2018) 275–280.

[76] X. Yuan, B. Wen, X. Ma, W. Zhu, X. Wang, S. Chen, et al., Enhancing the anaerobic digestion of lignocellulose of municipal solid waste using a microbial pretreatment method, Bioresour. Technol. 154 (2014) 1–9.

[77] M.P. Raut, J. Pandhal, P.C. Wright, Effective pretreatment of lignocellulosic co-substrates using barley straw-adapted microbial consortia to enhanced biomethanation by anaerobic digestion, Bioresour. Technol. 321 (2021) 124437.

[78] D. Wu, Z. Wei, Y. Zhao, X. Zhao, T.A. Mohamed, L. Zhu, et al., Improved lignocellulose degradation efficiency based on Fenton pretreatment during rice straw composting, Bioresour. Technol. 294 (2019) 122132.

[79] P. Alvira, M.J. Negro, M. Ballesteros, Effect of endoxylanase and α-L-arabinofuranosidase supplementation on the enzymatic hydrolysis of steam exploded wheat straw, Bioresour. Technol. 102 (2011) 4552–4558.

[80] R. Kumar, C.E. Wyman, Effects of cellulase and xylanase enzymes on the deconstruction of solids from pretreatment of poplar by leading technologies, Biotechnol. Prog. 25 (2010) 302–314.

[81] B. Parameswaran, K.U. Janu, R. Sindhu, A. Pandey, Hydrolysis of lignocellulosic biomass for bioethanol production, Biofuels 22 (2011) 229–250.

[82] M.D.L. Torre, R.M. Sampedro, Ú. Fillat, M.E. Eugenio, A. Blánquez, M. Hernández, et al., Comparison of the efficiency of bacterial and fungal laccases in delignification and detoxification of steam-pretreated lignocellulosic biomass for bioethanol production, J. Ind. Microbiol. Biotechnol. 44 (2017) 1561–1573.

[83] J.S. Schilling, J.P. Tewalt, S.M. Duncan, Synergy between pretreatment lignocellulose modifications and saccharification efficiency in two brown rot fungal systems, Appl. Microbiol. Biotechnol. 84 (2009) 465–475.

[84] H.K. Sharma, C. Xu, W. Qin, Biological pretreatment of lignocellulosic biomass for biofuels and bioproducts: an overview, Waste Biom. Valoriz. 10 (2019) 235–251.

[85] R. Sindhu, P. Binod, A. Pandey, Biological pretreatment of lignocellulosic biomass — an overview, Bioresour. Technol. 199 (2015) 76–82.

[86] S. Zhou, S. Raouche, S. Grisel, D. Navarro, J. Sigoillot, I. Gimbert, Solid-state fermentation in multi-well plates to assess pretreatment efficiency of rot fungi on lignocellulose biomass, Microb. Biotechnol. 8 (2015) 940–949.

[87] C. Wan, Y. Li, Fungal pretreatment of lignocellulosic biomass, Biotechnol. Adv. 30 (2012) 1447–1457.

[88] J. Zhang, Z. Zhu, X. Wang, N. Wang, W. Wang, J. Bao, Biodetoxification of toxins generated from lignocellulose pretreatment using a newly isolated fungus, *Amorphotheca resinae* ZN1, and the consequent ethanol fermentation, Biotechnol. Biofuels 3 (2010) 26.

[89] Y. Chen, L. Chai, C. Tang, Z. Yang, Y. Zheng, Y. Shi, et al., Kraft lignin biodegradation by Novosphingobium sp. B-7 and analysis of the degradation process, Bioresour. Technol. 123 (2012) 682–685.

[90] Y. Shi, L. Chai, C. Tang, Z. Yang, H. Zhang, R. Chen, et al., Characterization and genomic analysis of kraft lignin biodegradation by the beta-proteobacterium Cupriavidus basilensis B-8, Biotechnol. Biofuels 6 (2013) 1.

[91] Y. Shi, X. Yan, Q. Li, X. Wang, M. Liu, S. Xie, et al., Directed bioconversion of Kraft lignin to polyhydroxyalkanoate by Cupriavidus basilensis B-8 without any pretreatment, Process Biochem. 52 (2017) 238–242.

[92] J.S. Bak, M.D. Kim, I. Choi, K.H. Kim, Biological pretreatment of rice straw by fermenting with *Dichomitus squalens*, New Biotechnol. 27 (2010) 424–434.

[93] L. Wu, X. Li, Y. Liu, F. Yang, Q. Zhou, R. Ren, et al., Optimization of hydrothermal pretreatment conditions for mesophilic and thermophilic anaerobic digestion of high-solid sludge, Bioresour. Technol. 321 (2021) 124454.

[94] M. Camassola, A.J.P. Dillon, Effect of different pretreatment of sugar cane bagasse on cellulase and xylanases production by the mutant *Penicillium echinulatum* 9A02S1 grown in submerged culture, BioMed Res. Intl. (2014) 720–740.

[95] W. Zhang, Z. Yi, J. Huang, F. Li, B. Hao, M. Li, et al., Three lignocellulose features that distinctively affect biomass enzymatic digestibility under NaOH and $H_2SO_4$ pretreatments in Miscanthus, Bioresour. Technol. 130 (2013) 30–37.

[96] A.D. Moreno, D. Ibarra, P. Alvira, E.T. Pejo, M. Ballesteros, A review of biological delignification and detoxification methods for lignocellulosic bioethanol production, Crit. Rev. Biotechnol. (2015) 1–13.

[97] S. Roth, A.C. Spiess, Laccases for biorefinery applications: a critical review on challenges and perspectives, Bioprocess Biosyst. Eng. 38 (2015) 2285–2313.

[98] R.M. Javier, M.B. Claudio, S.Z. Laura, M.R.S. Francisco, D.G. Bruno, Inhibition of enzymatic hydrolysis of pretreated corn stover and sugar cane straw by laccases, Process Biochem. 67 (2018) 88–91.

[99] J. Chen, J. Xu, P. Huang, R. Sun, Effect of alkaline pretreatment on the preparation of regenerated lignocellulose fibers from bamboo stem, Cellulose 23 (2016) 1–13.

[100] D. Vásquez, E. Contreras, C. Palma, A. Carvajal, Thermochemical pretreatment of lignocellulose residues: assessment of the effect on operational conditions and their interactions on the characteristics of leachable fraction, Water Sci. Technol. 72 (2015) 1903–1911.

[101] H. Choi, J.S. Kwon, Multiscale modeling and predictive control of cellulose accessibility in alkaline pretreatment for enhanced glucose yield, Fuel 280 (2020) 118546.

[102] W. Wang, X. Wang, Y. Zhang, Q. Yu, X. Tan, X. Zhuang, et al., Effect of sodium hydroxide pretreatment on physicochemical changes and enzymatic hydrolysis of herbaceous and woody lignocelluloses, Indust. Crops Prod. 145 (2020) 112145.

[103] A. Mulyaningtyas, W.B. Sediawan, Effect of combined pretreatment of lignocellulose and the kinetics of its subsequent bioconversion by *Aspergillus niger*, Biocatal. Agric. Biotechnol. 21 (2019) 101292.

[104] Y. Su, R. Du, H. Guo, M. Cao, Q. Wu, R. Su, et al., Fractional pretreatment of lignocellulose by alkaline hydrogen peroxide: characterization of its major components, Food Bioprod. Process. 94 (2015) 322–330.

[105] W. Sympson, S.E. Nokes, A.N. Hickman, Recirculating calcium hydroxide solution: a practical choice for on-farm high solids lignocellulose pretreatment, Ind. Crop. Prod. 97 (2017) 492–497.

[106] M. Li, S. Si, B. Hao, Y. Zha, C. Wan, S. Hong, et al., Mild alkali-pretreatment effectively extracts guaiacyl-rich lignin for high lignocellulose digestibility coupled with largely diminishing yeast fermentation inhibitors in Miscanthus, Bioresour. Technol. 169 (2014) 447–454.

[107] J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P.F. Schatz, et al., Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl-propanoids, Phytochem. Rev. 2004 (3) (2004) 29–60.

[108] H. Sun, Y. Li, S. Feng, W. Zou, K. Guo, C. Fan, Analysis of fifive rice 4-coumarate: coenzyme A ligase enzyme activity and stress response for potential roles in lignin and flavonoid biosynthesis in rice, Biochem. Biophys. Res. Commun. 430 (2013) 1151–1156.
[109] Y. Zhu, J. Liu, W. Lv, Q. Pi, X. Zhang, L. Chen, et al., Revisiting alkaline pretreatment of lignocellulose: understanding the structural evolution of three components, Adv. Sustain. Syst. 4 (2020) 2000067.
[110] A. Goshadrou, K. Karimi, M.J. Taherzadeh, Improvement of sweet sorghum bagasse hydrolysis by alkali and acidic pretreatments, in: World Renewable Energy Congress – Sweden vol. 57, 2011, pp. 374–380.
[111] P. Jagannathan, C. Muthukumaran, K. Tamilarasan, A sequential pretreatment of lignocelluloses in bamboo biomass to fermentable sugars by acid/enzymatic hydrolysis, 3 Biotech 7 (2017) 260.
[112] D.A. Salvi, G.M. Aita, D. Robert, V. Bazan, Ethanol production from sorghum by a dilute ammonia pretreatment, J. Ind. Microbiol. 37 (2010) 27–34.
[113] Y.H. Jung, I.J. Kim, H.K. Kim, K.H. Kim, Dilute acid pretreatment of lignocellulose for whole slurry ethanol fermentation, Bioresour. Technol. 132 (2013) 109–114.
[114] X. Han, J. Bao, A general method on correcting the fluctuation of acid based pretreatment efficiency of lignocellulose for highly efficient bioconversion, ACS Sustain. Chem. Eng. 6 (2018).
[115] Y.H. Jung, H.M. Park, I.J. Kim, Y. Park, J. Seo, K.H. Kim, One-pot pretreatment, saccharifification and ethanol fermentation of lignocellulose based on acid–base mixture pretreatment, RSC Adv. 4 (2014) 55318–55327.
[116] M. Pedersen, K.S. Johansen, A.S. Meyer, Low temperature lignocellulose pretreatment: effects and interactions of pretreatment pH are critical for maximizing enzymatic monosaccharide yields from wheat straw, Biotechnol. Biofuels 4 (2011) 1–10.
[117] M. Pedersen, A.S. Meyer, Lignocellulose pretreatment severity – relating pH to biomatrix opening, New Biotechnol. 27 (2010) 739–750.
[118] X. Luo, R. Gleisner, S. Tian, J. Negron, W. Zhu, E. Horn, et al., Evaluation of mountain beetle-infested lodgepole pine for cellulosic ethanol production by sulfifite pretreatment to overcome recalcitrance of lignocellulose, Ind. Eng. Chem. Res. 2010 (49) (2010) 8258–8266.
[119] R. Zhu, V. Yadama, Effects of hot water extraction (HWE) of Douglas fir as a pre-process for the sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL), Holzforschung 71 (2016) 91–98.
[120] T.Q. Lan, R. Gleisner, J.Y. Zhu, B.S. Dien, R.E. Hector, High titer ethanol production from SPORL-pretreated lodgepole pine by simultaneous enzymatic saccharification and combined fermentation, Bioresour. Technol. 127 (2013) 291–297.
[121] H. Zhou, J.Y. Zhu, R. Gleisner, X. Qiu, E. Horn, J. Negrón, Pilot-scale demonstration of SPORL for bioconversion of lodgepole pine to bioethanol and lignosulfonate, Holzforschung 70 (2016) 21–30.
[122] L. Shuai, Q. Yang, J.Y. Zhu, F.C. Lu, P.J. Weimer, J. Ralph, et al., Comparative study of SPORL and dilute-acid pretreatments of spruce for cellulosic ethanol production, Bioresour. Technol. 101 (2010) 3106–3114.
[123] G.S. Wang, X.J. Pan, J.Y. Zhu, R. Gleisner, D. Rockwood, Sulfifite pretreatment to overcome recalcitrance of lignocellulose (SPORL) for robust enzymatic saccharification of hardwoods, Biotechnol. Prog. 25 (2009) 1086–1093.
[124] B. Cheng, X. Zhang, Q. Lin, F. Xin, R. Sun, X. Wang, et al., A new approach to recycle oxalic acid during lignocellulose pretreatment for xylose production, Biotechnol. Biofuels 11 (2018) 324.
[125] N.S. Mosier, A. Sarikaya, C.M. Ladisch, M.R. Ladisch, Characterization of dicarboxylic acids for cellulose hydrolysis, Biotechnol. Prog. 17 (2001) 474–480.
[126] A.M.J. Kootstra, N.S. Mosier, E.L. Scott, H.H. Beeftink, J.P.M. Sanders, Differential effects of mineral and organic acids on the kinetics of arabinose degradation under lignocellulose pretreatment conditions, Biochem. Eng. J. 43 (2009) 92–97.
[127] T.Q. Lana, S.R. Wanga, H. Lia, Y.Y. Qina, G.J. Yue, Effect of lignin isolated from p-toluenesulfonic acid pretreatment liquid of sugarcane bagasse on enzymatic hydrolysis of cellulose and cellulase adsorption, Indust. Crops Prod. 155 (2020) 112768.
[128] S.H. Lee, T.V. Doherty, R.J. Linhardt, J.S. Dordick, Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis, Biotechnol. Bioeng. 102 (2009) 1368–1376.
[129] T.D. Nguyen, K. Kim, S.J. Han, H.Y. Cho, J.W. Kim, S.M. Park, et al., Pretreatment of rice straw with ammonia and ionic liquid for lignocellulose conversion to fermentable sugars, Bioresour. Technol. 101 (2010) 7432–7438.
[130] K. Ninomiya, M. Abe, T. Tsukegi, K. Kuroda, Y. Tsuge, C. Ogino, et al., Lignocellulose nanofifibers prepared by ionic liquid pretreatment and subsequent mechanical nanofibrillation of bagasse powder: application to esterified bagasse/polypropylene composites, Carbohydr. Polym. 182 (2018) 8.
[131] S. Stolte, S. Steudte, A. Igartua, P. Stepnowski, The biodegradation of ionic liquids—the view from a chemical structure perspective, Curr. Org. Chem. 15 (2011) 1946–1973.
[132] S. Dong, B. Zhang, Y. Gao, X. Hu, An efficient process for pretreatment of lignocelluloses in functional ionic liquids, Int. J. Polym. Sci. 5 (2015) 1–6.
[133] G. Papa, T. Feldman, K.L. Sale, F. Adani, S. Singh, B.A. Simmons, Parametric study for the optimization of ionic liquid pretreatment of corn stover, Bioresour. Technol. 241 (2017) 627–637.
[134] T.V. Doherty, M.M. Pale, S.E. Foley, R.J. Linhardt, J. Dordick, S., Ionic liquid solvent properties as predictors of lignocellulose pretreatment efficacy, Green Chem. 12 (2010) 1967–1975.
[135] Z. Pang, W. Lyu, C. Dong, H. Li, G. Yang, High selective delignification using oxidative ionic liquid pretreatment at mild conditions for efficient enzymatic hydrolysis of lignocellulose, Bioresour. Technol. 214 (2016) 96–101.
[136] J. Wen, T. Yuan, S. Sun, F. Xu, R. Sun, Understanding the chemical transformations of lignin during ionic liquid pretreatment, Green Chem. 16 (2013) 181–190.
[137] S. Peleteiro, S. Rivas, J.L. Alonso, V. Santos, J.C. Parajó, Utilization of ionic liquids in lignocellulose biorefineries as agents for separation, derivatization, fractionation or pretreatment, J. Agric. Food Chem. 63 (2015) 8093–8102.
[138] X.D. Hou, T.J. Smith, N. Li, M.H. Zong, Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin, Biotechnol. Bioeng. 109 (2012) 2484–2493.
[139] X.D. Hou, J. Xu, N. Li, M.H. Zong, Effect of anion structures on cholinium ionic liquids pretreatment of rice straw and the subsequent enzymatic hydrolysis, Biotechnol. Bioeng. 112 (2015) 65–73.
[140] J. Xu, M.H. Zong, S.Y. Fu, N. Li, Correlation between physicochemical properties and enzymatic digestibility of rice straw pretreated with cholinium ionic liquids, ACS Sustain. Chem. Eng. 4 (2016) 4340–4345.
[141] Y. Cao, R. Zhang, T. Cheng, J. Guo, M. Xian, H. Liu, Imidazolium-based ionic liquids for cellulose pretreatment: recent progresses and future perspectives, Appl. Microbiol. Biotechnol. 101 (2017) 521–532.
[142] M. Moniruzzaman, K. Nakashima, N. Kamiya, M. Goto, Recent advances of enzymatic reactions in ionic liquids, Biochem. Eng. J. 2010 (48) (2010) 295–314.
[143] Y. An, M. Zong, S. Hu, N. Li, Effect of residual lignins present in cholinium ionic liquid-pretreated rice straw on the enzymatic hydrolysis of cellulose, Chem. Eng. Sci. 161 (2017) 48–56.
[144] M. Zhou, X. Ju, Z. Zhou, L. Yan, J. Chen, X. Yao, et al., Development of an immobilized cellulase system based on metal−organic frameworks for improving ionic liquid tolerance and *in situ* saccharification of bagasse, ACS Sustain. Chem. Eng. (2019) 19185–19193.
[145] Z. Chen, X. Bai, A. Lusi, C. Wan, High-solid lignocellulose processing enabled by natural deep eutectic solvent for lignin extraction and industrially relevant production of renewable chemicals, ACS Sustain. Chem. Eng. (2018) 6.
[146] A.A.N. Gunny, D. Arbain, E.M. Nashef, P. Jamal, Applicability evaluation of deep eutectic solvents–cellulase system for lignocellulose hydrolysis, Bioresour. Technol. 181 (2015) 297–302.
[147] W. Lim, A.A.N. Gunny, F.H. Kasim, I.M. AlNashef, D. Arbain, Alkaline deep eutectic solvent: a novel green solvent for lignocellulose pulping, Cellulose 26 (2019) 4085–4098.
[148] R. Wahlstrom, J. Hiltunen, M.P.S.N. Sirkka, S. Vuoti, K. Kruus, Comparison of three deep eutectic solvents and 1-ethyl-3-methylimidazolium acetate in the pretreatment of lignocellulose: effect on enzyme stability, lignocellulose digestibility and one-pot hydrolysis, RSC Adv. 6 (2016) 68100.
[149] A.A.N. Gunny, D. Arbain, M. Javed, N.B. Yazdi, S.C.B. Gopinath, P. Jamal, Deep eutectic solvents-halophilic cellulase system: an efficient route for in situ saccharification of lignocellulose, Process Biochem. 81 (2019) 99–103.
[150] Y. Wang, X. Meng, K. Jeong, S. Li, G. Leem, K.H. Kim, et al., Investigation of lignin-based deep eutectic solvent using p-hydroxybenzoic acid for efficient woody biomass conversion, ACS Sustain. Chem. Eng. 8 (2020) 12542–12553.
[151] L. Chen, Q. Yu, Q. Wang, W. Wang, W. Qi, X. Zhuang, et al., A novel deep eutectic solvent from lignin-derived acids for improving the enzymatic digestibility of herbal residues from cellulose, Cellulose 26 (2019) 1947–1959.
[152] A.P. Abbott, G. Frisch, J. Hartley, K.S. Ryder, Processing of metals and metal oxides using ionic liquids, Green Chem. 13 (2011) 471–481.
[153] Y.H. Choi, S.J. Van, Y. Dai, M. Verberne, F. Hollmann, I. Arends, et al., Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology? Plant Physiol. 156 (2011) 1701–1705.
[154] Y. Dai, S.J. Van, G.J. Witkamp, R. Verpoorte, Y.H. Choi, Natural deep eutectic solvents as new potential media for green technology, Anal. Chim. Acta 766 (2013) 61–68.
[155] A. Oliva, L.C. Tan, S. Papirio, G. Esposito, P.N.L. Lens, Effect of methanol-organosolv pretreatment on anaerobic digestion of lignocellulosic materials, Renew. Energy 169 (2021) 1000–1012.
[156] L. Qin, W. Li, J. Zhu, J. Liang, B. Li, Y. Yuan, Ethylenediamine pretreatment changes cellulose allomorph and lignin structure of lignocellulose at ambient pressure, Biotechnol. Biofuels 8 (2015) 174.
[157] T. Raj, K. Chandrasekhar, R. Banu, J.J. Yoon, G. Kumar, S.H. Kim, Synthesis of γ-valerolactone (GVL) and their applications for lignocellulosic deconstruction for sustainable green biorefineries, Fuel 303 (2021) 121333.
[158] Y. Jafari, H. Amiri, K. Karimi, Acetone pretreatment for improvement of acetone, butanol, and ethanol production from sweet sorghum bagasse, Appl. Energy 168 (2016) 216–225.
[159] J.A. Ferreira, M.J. Taherzadeh, Improving the economy of lignocellulose-based biorefifineries with organosolv pretreatment, Bioresour. Technol. 299 (2020) 122695.
[160] D. Hu, X. Ju, L. Li, C. Hu, L. Yan, T. Wu, Improved in situ saccharification of cellulose pretreated by dimethyl sulfoxide/ionic liquid using cellulase from a newly isolated *Paenibacillus* sp. LLZ1, Bioresour. Technol. 201 (2016) 8–14.
[161] R. Rinaldi, Instantaneous dissolution of cellulose in organic electrolyte solutions, Chem. Commun. 47 (2011) 511–513.
[162] P. Weerachanchai, J.M. Lee, Effect of organic solvent in ionic liquid on biomass pretreatment, ACS Sustain. Chem. Eng. 1 (2013) 894–902.
[163] A. Xu, Y. Zhang, Y. Zhao, J. Wang, Cellulose dissolution at ambient temperature: role of preferential solvation of cations of ionic liquids by a cosolvent, Carbohydr. Polym. 92 (2013) 540–544.
[164] F. Yao, F. Shen, X. Wan, C. Hu, High yield and high concentration glucose production from corncob residues after tetrahydrofuran + $H_2O$ co-solvent pretreatment and followed by enzymatic hydrolysis, Renew. Sust. Energ. Rev. 132 (2020) 110107.

[165] A. Lopatina, I. Anugwom, M. Esmaeili, L. Puro, T. Virtanen, M. Manttari, et al., Preparation of cellulose-rich membranes from wood: effect of wood pretreatment process on membrane performance, Cellulose 27 (2020) 9505–9523.

[166] N.L. Mai, S.H. Ha, Y. Koo, Efficient pretreatment of lignocellulose in ionic liquids/co-solvent for enzymatic hydrolysis enhancement into fermentable sugars, Process Biochem. 49 (2014) 1144–1151.

[167] S.S. Dukhin, C. Zhu, R. Dave, R. Pfeffer, J.J. Luo, F. Chávez, et al., Dynamic interfacial tension near critical point of a solvent–antisolvent mixture and laminar jet stabilization, Colloids Surf. A Physicochem. Eng. Aspects 229 (2003) 181–199.

[168] N. Sathitsuksanoh, M. Sawant, Q. Truong, J. Tan, C.G. Canlas, N. Sun, et al., How alkyl chain length of alcohols affects lignin fractionation and ionic liquid recycle during lignocellulose pretreatment, BioEnergy Res. 8 (2015) 973–981.

[169] J. Shi, K. Balamurugan, R. Parthasarathi, N. Sathitsuksanoh, S. Zhang, V. Stavila, et al., Understanding the role of water during ionic liquid pretreatment of lignocellulose: co-solvent or anti-solvent? Green Chem. 16 (2014) 3830–3840.

[170] M.M.S. Moretti, D.A.B. Martins, C.C.C. Nunes, M.A. Villena, O.M. Perrone, R. Silva, et al., Pretreatment of sugarcane bagasse with microwaves irradiation and its effects on the structure and on enzymatic hydrolysis, Appl. Energy 122 (2014) 189–195.

[171] J.S. Bak, Electron beam irradiation enhances the digestibility and fermentation yield of water-soaked lignocellulosic biomass, Biotechnol. Rep. 4 (2014) 30–33.

[172] B. Honnorat, V. Brüser, J.F. Kolb, Microwave plasma discharges for biomass pretreatment: degradation of a sodium carboxymethyl cellulose model, AIP Adv. 10 (2020), 095025.

[173] H. Li, Y. Qu, Y. Yang, S. Chang, J. Xu, Microwave irradiation — a green and efficient way to pretreat biomass, Bioresour. Technol. 199 (2015) 34–41.

[174] Y. Liu, L. Guo, L. Wang, W. Zhan, H. Zhou, Irradiation pretreatment facilitates the achievement of high total sugars concentration from lignocellulose biomass, Bioresour. Technol. 232 (2017) 270–277.

[175] Y. Liu, H. Zhou, L. Wang, S. Wang, L. Fan, Improving Saccharomyces cerevisiae growth against lignocellulose-derived inhibitors as well as maximizing ethanol production by a combination proposal of γ-irradiation pretreatment with in situ detoxification, Chem. Eng. J. 287 (2016) 302–312.

[176] C. Veluchamy, V.W. Raju, A.S. Kalamdhad, Electrohydrolysis pretreatment for enhanced methane production from lignocellulose waste pulp and paper mill sludge and its kinetics, Bioresour. Technol. 252 (2017) 52–58.

[177] G. Zhen, X. Lu, Y.Y. Li, Y. Zhao, Combined electrical-alkali pretreatment to increase the anaerobic hydrolysis rate of waste activated sludge during anaerobic digestion, Appl. Energy 128 (2014) 93–102.

[178] C. Veluchamy, V.W. Raju, A.S. Kalamdhad, Prerequisite — an electrohydrolysis pretreatment for anaerobic digestion of lignocellulose waste material, Bioresour. Technol. 235 (2017) 274–280.

[179] J. Gabhane, S.P.M.P. William, A.N. Vaidya, S. Das, S.R. Wate, Solar assisted alkali pretreatment of garden biomass: Effects on lignocellulose degradation, enzymatic hydrolysis, crystallinity and ultra-structural changes in lignocellulose, Waste Manag. 40 (2015) 92–99.

[180] M. Yasuda, A. Miura, R. Yuki, Y. Nakamura, T. Shiragami, Y. Ishii, et al., The effect of $TiO_2$-photocatalytic pretreatment on the biological production of ethanol from lignocelluloses, J. Photochem. Photobiol. A Chem. 220 (2011) 195–199.

[181] C. Lux, Z. Szalay, W. Beikircher, D. Kováčik, H.K. Pulker, Investigation of the plasma effects on wood after activation by diffuse coplanar surface barrier discharge, Eur. J. Wood Wood Prod. 71 (2013) 539–549.

[182] V. Jens, E. Thijs, V. Annick, S. Bert, Unconventional pretreatment of lignocellulose with low temperature plasma, Chemsuschem 10 (2016) 14–31.

[183] S.E.B. Schuette, J.V. Zurawski, J.M. Conway, P. Khatibi, D.L. Lewis, Q. Li, et al., Caldicellulosiruptor saccharolyticus transcriptomes reveal consequences of chemical pretreatment and genetic modifiication of lignocellulose, Microb. Biotechnol. 10 (2017) 1546–1557.

[184] N. Sathitsuksanoh, B. Xu, B. Zhao, Y.H.P. Zhang, Overcoming biomass recalcitrance by combining genetically modified switchgrass and cellulose solvent-based lignocellulose pretreatment, PLoS One 8 (2013), e73523.

[185] N.N. Tran, M.E. Gelonch, S. Liang, Z. Xiao, M.M. Sarafraz, M. Tisma, et al., Enzymatic pretreatment of recycled grease trap waste in batch and continuous-flow reactors for biodiesel production, Chem. Eng. J. 426 (2021) 131703.

[186] Y.C. Park, T.H. Kim, J.S. Kim, Flow-through pretreatment of corn stover by recycling organosolv to reduce waste solvent, Energies 11 (2018) 879.

[187] H.A. Ruiz, M. Conrad, S.N. Sun, A. Sanchez, G.J.M. Rocha, A. Romaní, E. Castro, et al., Engineering aspects of hydrothermal pretreatment: from batch to continuous operation, scale-up and pilot reactor under biorefinery concept, Bioresour. Technol. 299 (2020) 122685.

[188] I. Jaramillo, A. Sanchez, Mass flow dynamic modeling and residence time control of a continuous tubular reactor for biomass pretreatment, ACS Sustain. Chem. Eng. 6 (2018) 8570–8577.

[189] F. Rodríguez, A. Sanchez, L. Amaya-Delgado, Xylooligosaccharides production from lignocellulosic biomass using a pilot-scale pretreatment continuous tubular reactor. Modelling and experimental validation, Indus. Crops Prod. 134 (2019) 62–70.

[190] C. Liu, C.E. Wyman, The effect of flow rate of compressed hot water on xylan, lignin, and total mass removal from corn stover, Indust. Eng. Chem. Res. 42 (2003) 5409–5416.

[191] H. Fang, J. Deng, X. Zhang, Continuous steam explosion of wheat straw by high pressure mechanical refining system to produce sugars for bioconversion, Bioresources 6 (2011) 4468–4480.

[192] L. Zhang, Y. Pu, J.R. Cort, A.J. Ragauskas, B. Yang, Revealing the molecular structural transformation of hardwood and softwood in dilute acid flowthrough pretreatment, ACS Sustain. Chem. Eng. 4 (2016) 6618–6628.

[193] A.S.A. da Silva, R.S.S. Teixeira, T. Endo, E.P.S. Bon, S.H. Lee, Continuous pretreatment of sugarcane bagasse at high loading in an ionic liquid using a twinscrew extruder, Green Chem. 15 (2013) 1991–2001.

[194] C. Løhre, M. Kleinert, T. Barth, Organosolv extraction of softwood combined with lignin-to-liquid-solvolysis as a semi-continuous percolation reactor, Biomass Bioenergy 99 (2017) 147–155.

[195] C. Liu, C.E. Wyman, The effect of flow rate of very dilute sulfuric acid on xylan, lignin, and total mass removal from corn stover, Indust. Eng Chem. Res. 43 (2004) 2781–2788.

[196] H.L. Trajano, N.L. Engle, M. Foston, A.J. Ragauskas, T.J. Tschaplinski, C. E. Wyman, The fate of lignin during hydrothermal pretreatment, Biotechnol. Biofuels 6 (2013) 110.

[197] S. Bhagia, H. Li, X. Gao, R. Kumar, C.E. Wyman, Flowthrough pretreatment with very dilute acid provides insights into high lignin contribution to biomass recalcitrance, Biotechnol. Biofuels 9 (2016) 245.

[198] J.A. Perez-Pimienta, G. Papa, J.M. Gladden, B.A. Simmons, A. Sanchez, The effect of continuous tubular reactor technologies on the pretreatment of lignocellulosic biomass at pilot-scale for bioethanol production, RSC Adv. 10 (2020) 18147–18159.

[199] T.H. Kim, C.H. Choi, K.K. Oh, Bioconversion of sawdust into ethanol using dilute sulfuric acid-assisted continuous twin screw-driven reactor pretreatment and fed-batch simultaneous saccharification and fermentation, Bioresour. Technol. 130 (2013) 306–313.

[200] Y.S. Cheng, P. Mutrakulcharoen, S. Chuetor, K. Cheenkachorm, P. Tantayoutai, E. J. Panakkal, et al., Recent situation and progress in biorefining process of lignocellulosic biomass: toward green economy, Appl. Sci. Eng. Progr. (2020) 13.

[201] D. Kumar, G.S. Murthy, Impact of pretreatment and downstream processing technologies on economics and energy in cellulosic ethanol production, Biotechnol. Biofuels 4 (2011) 27.

[202] M. Zhou, L. Yan, H. Chen, X. Ju, Z. Zhou, L. Li, Development of functionalized metal-organic frameworks immobilized cellulase with enhanced tolerance of aqueous-ionic liquid media for in situ saccharification of bagasse, Fuel 304 (2021) 121484.

[203] S. Jin, M. Gao, W. Kong, B. Yang, H. Kuang, B. Yang, et al., Enhanced and sustainable pretreatment for bioconversion and extraction of resveratrol from peanut skin using ultrasound-assisted surfactant aqueous system with microbial consortia immobilized on cellulose, 3 Biotech 10 (2020) 1–9.

[204] H. Liu, J. Sun, S.Y. Leu, S. Chen, Toward a fundamental understanding of cellulase-lignin interactions in the whole slurry enzymatic saccharification process, Biofuels Bioprod. Biorefin. 10 (2016).

[205] Y. Zhou, X. Zhao, D. Liu, Effects of non-ionic surfactant on the enzymatic hydrolysis of lignocellulose and corresponding mechanism, Progr. Chem. 27 (2015) 1555–1565.

[206] Y.A. Chen, Z. Yan, Y. Qin, D. Liu, X. Zhao, Evaluation of the action of Tween 20 non-ionic surfactant during enzymatic hydrolysis of lignocellulose: pretreatment, hydrolysis conditions and lignin structure, Bioresour. Technol. 269 (2018) 329–338.

[207] X.D. Hou, N. Li, M.H. Zong, Renewable bio ionic liquids-water mixtures mediated selective removal of lignin from rice straw: visualization of changes in composition and cell wall structure, Biotechnol. Bioeng. 110 (2013) 1895–1902.

[208] J. Zhang, W. Shen, C. Collings, K.A.V. Meulen, B.G. Fox, L.M.V. Ramos, et al., Visualizing plant cell wall changes proves the superiority of hydrochloric acid over sulfuric acid catalyzed γ-valerolactone pretreatment, Chem. Eng. J. 412 (2021) 128660.

[209] S.Y. Ding, Y.S. Liu, Y. Zeng, M.E. Himmel, J.O. Baker, E.A. Bayer, How does plant cell wall nanoscale architecture correlate with enzymatic digestibility? Science 338 (2012) 1055.

[210] M. Dong, S. Wang, F. Xu, J. Wang, N. Yang, Q. Li, et al., Pretreatment of sweet sorghum straw and its enzymatic digestion: insight into the structural changes and visualization of hydrolysis process, Biotechnol. Biofuels 12 (2019) 276.

[211] X. Li, J. Sha, Y. Xia, K. Sheng, Y. Liu, Y. He, Quantitative visualization of subcellular lignocellulose revealing the mechanism of alkali pretreatment to promote methane production of rice straw, Biotechnol. Biofuels 13 (2020).