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ABSTRACT

In analogue to the biorefinery concept, the separation process of lignocellulosic biomass is the most critical step to obtain its main components, namely cellulose, hemicelluloses and lignin. Moreover, the applied fractionation approach has a decisive impact on the characteristics and subsequent valorization strategies of the distinguished fractions. This review presents the state of art of novel biomass fractionation processes that are recently developed and focusing on autohydrolysis, organosolv fractionation, ionic liquid and deep eutectic solvent (DES) treatment. Moreover, the facing challenges, perspectives and future development direction in the field of fractionation of lignocellulosic biomass are discussed. The purpose of this review is to provide inspiration and guidance for fractionating biomass with environmentally friendly and efficient pathways, thus to push forward their further industrialization based on the integrated biorefinery concept.

1. Introduction

Currently, the enormous usage of fossil fuels due to increasing industrialization has led to serious environmental problems, such as climate change, as well as air and water pollution (Usmani et al., 2021). The urgent need to explore sustainable resources as alternatives and develop green process to meet the increasing energy demand has attracted extensive attention. Lignocellulosic biomass, composed of polysaccharides, lignin and small quantities of other compounds such as pectins, proteins, extractives and ash, is one of the most promising resources to tackle the challenges by providing sustainable and green energy systems (Maity, 2015; Usmani et al., 2021). This is not only because its amount is abundant, but also because the integrated utilization of lignocellulosic biomass is expected to contribute to revitalizing the traditional forest products industries, such as the pulp and papermaking industry. To overcome the disadvantages of traditional forest products industries focusing on cellulose fibers as the main product, it is of great significance that lignocellulosic biomass is considered as raw materials to produce various biochemicals or biomaterials (Banu et al., 2021; Mankar et al., 2021).

Based on the concept of biorefinery, it is clear that the most important distinguishing features of biorefinery are the numerous and various types of biobased products (Banu et al., 2021; Usmani et al., 2021; Yan et al., 2021). Generally, an integrated biorefinery involves multi-step processes, in which the first step is conventionally referred to as fractionation of biomass. In this step the feedstock is fractionated into its main distinguished components (Peng and She, 2014; Zhang et al., 2018a). Afterwards, the obtained biomass components are used in further conversion processes, in which the outputs can be converted into commercialized products (Zhang et al., 2019b).

Though the definition of various fractionation technologies is different, it is clear that the fractionation process should realize the selective separation of biomass components. The traditional separation processes for lignocellulosic materials, including the Kraft, Sulfite, and Soda processes, have been studied extensively and commercialized (Figueiredo et al., 2018). Many other novel protocols, such as autohydrolysis, organosolv, deep eutectic solvent (DES) and ionic liquid treatment, which provide environmentally friendly and efficient pathways to separate lignocellulosic biomass into valuable fractions, have also been developed based on the integrated biorefinery concept. A considerable number of published reviews summarized and discussed these fractionation processes of lignocellulosic biomass. However, most

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of them focus on their process optimization, mechanism, and further valorization of the isolated biopolymers. As is known to all, the ultimate goal of these emerging fractionation processes is to achieve industrialization and generate high-value bioproducts. Although many efforts on bridging the gap between laboratory research and commercialization have been done, only a few of these novel fractionation processes enter the stage of pilot scale or industrialization. Therefore, the recent improvments and faced improlems affecting their performance should be updated. In this review, we summarized and discussed the advances, critical technical challenges, perspectives and future development direction of those novel fractionation process in recent years towards to their further industrialization.

2. Organosolv fractionation

Recently, new biorefinery technologies based on organosolv fractionation were developed to separate cellulose, lignin, and hemicellulosic sugars from lignocellulosic biomass (Delmas, 2008). Importantly, the organic solvents are able to be recovered and reused easily. Such an environment-friendly approach particularly also provides the possibility of developing these three components of lignocellulose in the high-value applications (Bozell et al., 2011; Jahan et al., 2007).

2.1. Process of alcohol fractionation

Novel fractionation processes using organic solvents, especially alcohols and organic acids, have exhibited excellent performance to selective separation of lignocellulosic biomass (Reisinger et al., 2014; Villaverde et al., 2012). During recent decades, volatile alcohols with low boiling point have been widely reported as the organic solvent to fractionate lignocellulosic biomass in organosolv processes. Among those alcohols, ethanol and methanol have been frequently adopted because of their low-budget and low toxicity (Zhao et al., 2009). During the fractionation processes, the reaction temperature usually is above 160 °C during the process with the time of 30–90 min (Zhang et al., 2016). The process parameters depend on the chosen raw material, solvent and delignification degree. The organosolv fractionation processes using these two orgainc solvents (ethanol and methanol) are presented in Table 1. These processes can also be conducted using an aqueous solution of alcohols with catalysts. The addition of inorganic acid used as catalysts could contribute to the separation of the lignocellulose, but it can also result in an excessive degradation of hemicelluloses and the enhancement of the production of furfural and HMF (Amiri and Karimi, 2015; Wei et al., 2017). Some organosolv processes based on alcohols, such as ASAM (alkali-sulfite-anthraquinone-methanol) and ALCELL (ethanol-water), have been conducted at a pilot-plant or industrial scale, but these processes have not been successful in replacing the Kraft process. The integrated strategies to combine ethanol fractionation and pretreatment technologies, including enzymatic pretreatment and autohydrolysis, were also applied to fractionate lignocellulose (Chen et al., 2015; Weinwurm et al., 2017). Both pretreatment processes facilitate the subsequent delignification by enhancing cleavages of aryl-ether bonds.

Typically, the cellulose fiber is the raw material for the production of pulp and dissolving pulp. It is also a feedstock for the production of chemicals and biofuels such as glucose, ethanol, or butanol, using fermentation and enzymatic hydrolysis. It has been proven that the ethanol fractionation of lignocellulosic biomass has beneficial effects on the subsequent enzymatic hydrolysis and fermentation of cellulose to obtain glucose and ethanol (Amiri and Karimi, 2015; Salapa et al., 2017; Zhang and Wu, 2014). The extracted lignin through organosolv fractionation presents high purity and abundant functional groups, which is considered as an alternative feedstock with the focus to generate valuable products (Huijgen et al., 2014; Zijlstra et al., 2020).

Table 1
Fractionation process with ethanol and methanol.

Fractionation reagent	Raw material	Fractionation conditions (T: temperature; t: time; L/S: liquid/solid ratio)	Main outcome	Ref.
60% ethanol	*Eucalyptus globulus*	T:180–200 °C; t: 30–120 min; L/S: 6/1	Cellulose-to-glucose: 69–77%; Glucose to ethanol conversion yield: 51%	(Muñoz et al., 2011)
75% ethanol and 1% H$_2$SO$_4$	Pine and elm	T: 150–180 °C; t: 30–60 min; L/S: 8/1	Ethanol yield: 14.2–87.9 g/ kg of pine; 70.1–121.2 g/ kg of elm	(Amiri and Karimi, 2015)
50% ethanol and 0.4% HCl	*Chamaecyparis obtusa*	T: 170 °C; t: 45 min; L/S: 5.3/1	Cellulose-to-glucose: 70%	(Hideno et al., 2013)
60% ethanol and 5% acetic acid	Sugarcane bagasse	T: 190 °C; t: 45 min; L/S: 8/1	Xylose yield: 11.83%; Cellulose conversion yield: 93.8%	(Zhang and Wu, 2014)
65% methanol	Pressed pericarp fibers	T: 180 °C; t: 75 min; L/S: 8/1	Lignin removal: 44.6%; Glucose yield: 42.5%	(Hii et al., 2012)
45% methanol and 3% H$_2$SO$_4$	Hemp hurds	T: 165 °C; t: 20 min; L/S: 25/1	Hemicellulose removal: 75%; Lignin removal: 75%; Cellulose-to-glucose conversion yield: 60% after enzymatic hydrolysis	(Gandolfi et al., 2014)
organocell process (70% Methano and 1% NaOH)	*Populus tomentosa Carr*	T: 80 °C; t: 5 h	Cellulose 80.3%	(Wang et al., 2012b)

2.2. Process of organic acid fractionation

Although alcohols fractionation can efficiently separate lignocellulosic biomass, it needs a high temperature and a long holding time to achieve efficient delignification (Li et al., 2016). In this case, some fatty acids with short-chain including formic, and acetic acids have been applied to biomass fractionation due to their good delignification selectivity (Li et al., 2016). The typical flowchart of organic acid fractionation is shown in Fig. 1. After fractionation, the crude cellulose pulp and spent liquor are filtrated, and then the solids are washed with hot organic acid to avoid precipitation of the dissolved lignin on the fiber surface. The high-purity cellulose is obtained after further water washing and subsequent screening. Spent liquor, including the filtrate and the organic acid washings, can be evaporated to recover recyclable concentrated residues and organic solvent, which is further separated into lignin and hemicelluloses by adding water.

As shown in Table 2, the organosolv fractionation with a high concentration of organic acid can be operated under mild conditions depended on its inherent advantages, such as high acidity and its Hildebrand's solubility value being close to that of lignin (Zhao et al., 2009). In those processes, various catalysts, including inorganic hydrochloric acid (HCl), sulfuric acid (H$_2$SO$_4$) and oxidizing agents
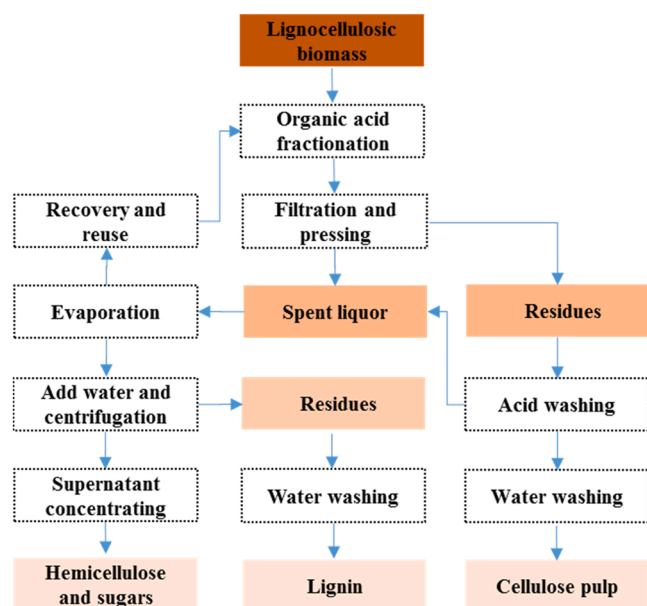
Fig. 1. Overview of organic acid fractionation of lignocellulosic biomass.

Table 2
Organic acid fractionation processes.

Fractionation reagent	Raw material	Fractionation conditions (T: temperature; t: time; L/S: liquid/solid ratio)	Main result	Ref.
85% formic acid	Bamboo	T: 145 °C; t: 45 min; L/S: 7/1	Pulp yield: 42.2%; Lignin removal: 95.25%	(Zhang et al., 2018a)
88% formic acid	Bamboo	T: 101 °C; t: 2 h; L/S: 20/1	Pulp yield: 52.8%; Lignin removal: 80.4%	(Li et al., 2012)
88% formic acid and 3% H_2O_2 (Milox method)	Bamboo	Step 1: formic acid, T: boiling point, t: 1 h, L/S: 20/1; Step 2: adding 3% H_2O_2, T: 101 °C, t: 2 h; Step 3: T: boiling point, t: 1 h	Pulp yield 48.7%; Lignin removal: 88.9%	(Li et al., 2012)
88% formic acid and 3% H_2O_2	Bamboo	T: 101 °C; t: 2 h; L/S: 20/1	Pulp yield 48.1%; Lignin removal: 87.9%	(Li et al., 2012)
88% formic acid and 1% HCl	Bamboo	T: 101 °C; t: 2 h; L/S: 20/1	Pulp yield 51.7%; Lignin removal: 79.1%	(Li et al., 2012)
78% formic acid and 0.1% H_2SO_4	Sugarcane bagasse	T: 107 °C; t: 1.5 h; L/S: 10/1	Pulp yield 48.2%; Lignin removal: 87.3%	(Zhao and Liu, 2012)
86.25% acetic acid and 0.25% HCl	Empty fruit bunches	T: boiling point; t: 2 h (Acetosolv method)	Pulp yield: 46.56%; Lignin removal: and 89.7%	(Ferrer et al., 2013)
50% acetic acid, 30% formic acid and 20% water	*Miscanthus × giganteus*	T: 107 °C; t: 3 h (Formacell method)	Lignin removal: 86.5%	(Vanderghem et al., 2011)
acetic acid, formic acid and H_2O_2	Wheat straw	First step: acetic acid and formic acid (65/35 mass ratio, 85% in water), L/S: 8/1, T: 105 °C, t: 3 h; Second step: 10% H_2O_2 on dry matter raw pulp, T: 85 °C, t: 90 min	Pulp yield: 48%; hemicellulosic fractions 27%; lignin yield: 21%	(Snelders et al., 2014)
20–60% peracetic acid	Sugarcane bagasse	T: 70–90 °C; t: 2 h; L/S: 3/1–7/1	Lignin removal: 80%	(Zhao et al., 2007)

(H_2O_2), are usually added to assist the delignification during organic acid fractionation, especially in acetic acid treatment. Various organic acid fractionation processes, such as the Milox (Li et al., 2012), Formacell (Vanderghem et al., 2011), and Acetosolv (Ferrer et al., 2013) methods, have been developed, and applied to different biomass materials including hardwoods (Dapia et al., 2002), softwoods (Shao et al., 2020), and non-woods (Zhang et al., 2018a). It is reported that organic acid fractionation using acetic and formic acid at 105 °C for 3 h exhibited efficient removal of lignin for wheat straw (Snelders et al., 2014). 85% lignin removal can be achieved from rice straw by formic acid fractionation at 100 °C for 60 min (Lam et al., 2001). However, most of fractionation processes using the organic acid are performed at the relatively mild conditions with an atmospheric pressure and a low temperature, which hinder efficient delignification. To further enhance the delignification degree, the reaction time of the whole process had to be extended. It was reported that one-step formic acid-based organosolv fractionation process under pressure (0.3 MPa, at 145 °C for 45 min) was developed to convert bamboo (*Neosinocalamus affinis*) in its main components, which provided a high efficient method to produce cellulose pulp (42.2%), lignin (31.5%), hemicellulose-rich fraction (8.5%), 3.56% furfural, and 3.80% acetic acid (Zhang et al., 2018a). This strategy of fractionation performed under pressure shows a super-efficient delignification way to produce cellulose, lignin, and hemicellulosic sugars, compared with these processes under atmospheric conditions with or without catalysis. 95.25% of lignin could be removed from raw materials which was significantly higher than the lignin removal rate (80.4%) from the formic acid fractionation process under atmospheric conditions (Li et al., 2012; Zhang et al., 2018a). Therefore, one-step formic acid fractionation process under pressure could contribute significantly to achieve its industrialization.

2.3. Challenge and outlook of organosolv fractionation

As one of the most studied organosolv fractionation processes, organic acid fractionation has been considered as a promising alternative to traditional pulping technology, because satisfying cellulose pulp yield and effective delignification with simultaneous hemicelluloses degradation can be achieved (Li et al., 2012). The obtained main fractions can be further converted into various biochemicals and biomaterials (Kupiainen et al., 2012). Furthermore, organic acid fractionation also opens the possibility of using the lignin for high-value

applications. Based on the dissolved lignin obtained from formic acid fractionation, the spherical nanoparticles with a uniform particle size distribution could be prepared. Additionally, the cellulose nanocrystals (CNCs) was easily prepared from the cellulose via TEMPO oxidation, which can mix with lignin-NPs to form nanocomposite films (Zhang et al., 2019b).

Yet, some issues still perplex researchers in the current fractionation. The faced major challendge for organic acid fractionation is the

corrosion risk, thererfore anti-corrosion equipment is required during the whole process. Large amounts of wastewater containing low-concentration organic solvents produced in the water washing process of cellulose solid is another bottleneck, in that recovery of organic solvents from the washings is difficult and needs to capture the large production costs. Direct drying process of cellulose solid produced from organic solvent washing maybe provide a meaningful choice for the industrialization of organosolv fractionation. Organosolv fractionation aims at the full utilization of the main biomass components based on the integrated biorefinery. To date, numerous researches focus on the enzymatic hydrolysis and fermentation of the polysaccharides fraction obtained from organosolv fractionation, especially ethanol-based fractionation. Other conversion pathways for the obtained cellulose, such as the preparation of nano-functional materials, are relatively less reported. Furthermore, the organosolv lignin presents great potential due to its special structural properties, it has not been developed up to a commercial level towards the new materials and chemicals yet.

3. Hydrolysis of biomass with hydronium ions

3.1. Autohydrolysis

As shown in Fig. 2, autohydrolysis pretreatment and acid-catalyzed hydrolysis belong to a fractionation process in which hydronium ions break down the linkages in cellulose, hemicelluloses, and lignin, which can be performed alone or in combination. As an economically feasible and environment-friendly process, autohydrolysis, namely hot water pretreatment, is applied to selectively extract hemicelluloses before subsequent pulping processes (Ligero et al., 2011; Zhang et al., 2018b). The whole process is catalyzed by hydronium ions, which is mainly produced from the formed acetic acid by the cleavage of acetyl groups (Ruiz et al., 2012). A liquid phase rich in hemicelluloses-derived products can be obtained without significant modifications to lignin and leaving cellulose in the solid material. Subsequently, sugars were degraded from hemicelluloses and recovered in a liquid phase (Garrote et al., 2001). Meanwhile, the remained cellulose and lignin in solid phase can further be fractionalized and conversed (Kim et al., 2009; Laser et al., 2002). A Finnish company named CH-Bioforce Oy built an automated pilot production line which could extract hemicelluloses in high yield and purity in their native polymeric form by using vacuum and ensuring precise chemical control. Recently, it has been demonstrated that biomass autohydrolysis is beneficial for the subsequent Kraft pulping by increasing the lignin's solubility (Lu et al., 2012). Also, an integrated fractionation process for bamboo chips which combined autohydrolysis and formic acid treatment has been explored, which allowed to achieve a high yield of oligosaccharide, cellulose fibers and high-purity lignin (Zhang et al., 2018b).

3.2. Acid-catalyzed hydrolysis

Acid-catalyzed hydrolysis, such as dilute sulfuric acid hydrolysis, has

been widely used as a pretreatment process of lignocellulosic biomass, which can promote efficient saccharification of biomass to fermentable sugars for the production of bioethanol (Kim et al., 2000; Nguyen et al., 2000). Other inorganic acids, including hydrochloric acid (Goldstein and Easter, 1992), nitric acid (Brink, 1993), and phosphoric acid (Israilides et al., 1978), have also been studied. It is reported that the dilute sulfuric acid pretreatment can result in removal of hemicelluloses to a high extent and significantly enhance the accessibility of cellulose in the subsequent enzymatic hydrolysis (Esteghlalian et al., 1997). The released sugars from hemicelluloses by the dilute-acid pretreatment are usually recoverable. Recently, dilute-acid hydrolysis processes have been developed to obtain a high conversion yield of xylan/xylose using mild conditions, which is beneficial to achieve favorable economics process (Hinman et al., 1992).

After acid pretreatment (Fig. 2), the obtained hemicellulosic sugars and pretreated cellulosic solids can be further converted by acid catalytic hydrolysis. It's a conventional technology to convert hemicelluloses and cellulose into intermediate platform chemicals, including furfural, glucose, levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) (Alvira et al., 2010; Hayes et al., 2008; Pileidis and Titirici, 2016; Saha and Abu-Omar, 2014; Wang et al., 2014). The hemicellulosic sugars, which is mainly composed of xylose, can be used to prepare furfural, while cellulose is hydrolyzed to HMF, glucose and LA. Dilute sulfuric acid also has been applied to commercially manufacture furfural, which is achieved by hydrolyzing hemicelluloses to sugars and then futher degraded into furfural (Zeitsch, 2000). Jeong et al. (2017) adopted a two-step dilute sulfuric acid hydrolusis of *Quercus mongolica* with the temperature range of 100–230 °C to produce pentoses sugars and LA.

3.3. Challenge and outlook of acid-catalyzed hydrolysis

Some of the key challenges of the acid hydrolysis process for biomass, involving environment, economy, versatility, and efficiency, limit its utilization in large-scale processes. Among most of the conventional acid hydrolysis processes, the recycling of the acid catalyst, product separation, and equipment corrosion are the main drawbacks. The usage of solid acid catalysts exhibits excellent peformence to breakthrough some of these difficulties due to high selectivity, efficient activity, long catalyst life, and mild operating conditions (Guo et al., 2012). Various solid acids used for biomass hydrolysis are explored such as transition-metal oxides, H-form zeolites, cation-exchange resins, supported solid acids and heteropoly compounds (Guo et al., 2012). Among these solid acids, carbonaceous solid acid catalysts can provide abundant acidic sites of SO_3H groups touched by reactants and are considered as the most promising catalyst for the hydrolysis of cellulose (Lou et al., 2008; Shu et al., 2010; Zong et al., 2007). Fukuhara et al. (2011) reported that a cellulose-derived carbon-based solid acid presented high catalytic performance for cellulose hydrolysis. High glucose yields of 75% with 80% selectivity were obtained at 150 °C with the reaction time of 24 h. However, solid catalysts cannot be easily
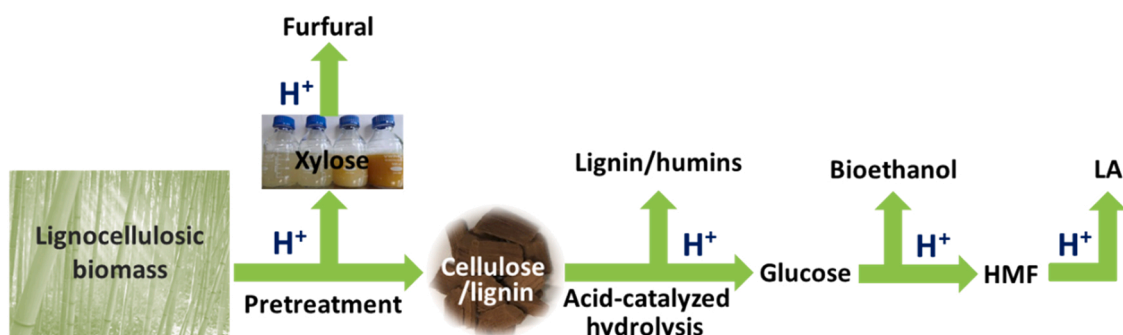

Fig. 2. Roadmap for acid-catalytic hydrolysis of lignocellulosic biomass for the production of high-value product.

separated from the un-hydrolyzed solid residues due to their similar physical form. The use of solid catalysts designed with magnetic property is one way to improve its separation and reuse. The hydrolysis of β-1,4-glucan used magnetic solid acid with mesoporous structure could produce a glucose yield as high as 96% from cellobiose, while a glucose yield of 50% was produced from amorphous cellulose with a conventional solid acid. It also exhibited good hydrothermal stability and can be recycled when placed in a magnetic field (Lai et al., 2011).

During autohydrolysis and acid-catalyzed hydrolysis, most of the hemicelluloses could be extracted from biomass materials, while parts of lignin and lignin-carbohydrate complexes (LCCs) were also degraded and dissolved. It has been demonstrated that LCCs have a negative effect on separating and recovering the dissolved hemicellulosic sugars as well as the subsequent enzymatic hydrolysis (Himmel et al., 2007; You et al., 2015). In the past few decades, numerous studies have focused on the extraction, purification and further valorization process of hemicellulosic sugars. However, lignin and LCCs recovered from extraction liquid have shown promising application prospects, especialy in medicine and cosmetic fileds, duo to their excellent pharmacological activities and antioxidant performance (Min et al., 2014; Niu et al., 2016; Sakagami and Matsuta, 2013; You et al., 2015; Zhang et al., 2019a).

4. Ionic liquid fractionation

Ionic liquids are defined as salts composed of organic cations, such as imidazoles, alkyl quaternary ammonium salts, alkyl quaternary phosphoniums and some inorganic anions, which might be liquid, powdery or solid at room temperature (Brandt et al., 2013). Among numerous reported researches, the common types of the cations and anions of ionic liquids are shown in Table 3. Generally, the ionic liquids have a high viscosity, and its viscosity would decrease as the temperature increases. As a new green solvent, ionic liquid has many excellent characteristics, such as low volatility, wide-range change of melting point, high electrochemical application value (Das et al., 2020). Ionic liquids can be easily recycled and has good solubility on organic substance, and owns less solvent loss in the recovery process at the same time (Chiappe et al., 2017). Besides, the molecular design of ionic liquids can be designed according to different requires (Domańska and Królikowski, 2012), it also has no pollution. Recently, ionic liquids have been considered as potential solvents for lignocellulosic biomass fractionation.

4.1. The influencing factors of ionic liquid fractionation

Previous studies demonstrated that the ionic liquids are extremely efficient for solving the problem of "biomass recalcitrance" and selectively dissolving either or all lignocellulosic components (Khoo et al., 2020). Both the polar and nonpolar groups of ionic liquids are beneficial for dissolving the lignocellulosic biomass, therefore selecting the appropriate anion and cation species is critical due to the coordination of hydrogen bonding in these components (Bhatia et al., 2020). Cellulose could be precipitated and further separated from the solution containing

dissolved cellulose and lignin by adding anti-solvent water (Wang et al., 2012a).

According to the previous studies, the cation size as well as its functional groups have an important effect on dissolving the lignoncellulosic biomass. Cellulose can more easily be dissolved in small cations because of the steric hindrance effect preventing the formation of hydrogen bonding between large molecule and cellulose (Alayoubi et al., 2020). The process parameters also play a significant role on dissolving biomass components (Khoo et al., 2020; Liu et al., 2019). Increasing the reaction time and temperature could contribute to the dissolution of lignocellulose, which is very important for producing the regenerated lignocellulosic materials. In recent years, many researchers focused on the investigation of ionic liquid-water binary system to improve the solvent system. The introduction of water plays a positive role on the pretreatment of biomass via ionic liquid technology, as the ionic liquid-water system has a higher solubility than the pure ionic liquid. The addition of water could not only decrease the viscosity of ionic liquid, but also greatly reduce its production cost, which is beneficial for realizing the recovery and reuse of ionic liquid and simplify the recovery process. Cha et al. (2014) studied the intermolecular interaction in the ionic liquid (1-butyl-3-methylimidazolium)-aqueous solution. The results showed that the cations and anions of halogenated ionic liquid could interact with each other due to the hydrogen bonding and Coulomb force, while the addition of water could dissociate the anions and cations (Cha et al., 2014). It has been proven that the addition of salts could help in deconstructing and increasing the selectivity of biomass fractionation (Ab Rahim et al., 2020; Kohli et al., 2020). Besides, the assisted technologies, including the ultrasound and microwave processing and the adjustment of pH value of solution, could significantly enhance the solubility of biomass components during ionic liquid fractionation (Pang et al., 2016).

The dissolution of cellulose in ionic liquids can be explained by the formation of hydrogen bonding between anions and -OH group of cellulose. Although the delignification mechanism during ionic liquid fractionation is not completely clear, it is generally accepted that the dissolution of lignin in the ionic liquids is closely related with the π–π interactions, the hydrogen-bonding basicity of the anions and acidity of the cations (Akiba et al., 2017; Chu and He, 2019; Hart et al., 2014; Zhu et al., 2018). The lignin structure was hydrolyzed in the ionic liquid, and the ether bond such as β-O-4 could be broken, and the molecular weight decreased obviously.

4.2. Challenges and perspectives of ionic liquid fractionation

The numerous literature reports on this field demonstrate the enormous potential of ionic liquids fractionation. Although there is significant progress in the direct fractionation of biomass using ionic liquids, challenges existed in different treatment methods limit their commercial applications, which must be overcome in the following directions:

1. The reaction solution from the fractionation process comprises of ionic liquids, lignin, hemicellulosic fractions and water. Recycling property of ionic liquids for biomass fractionation is a crucial factor in order to maintain the economic efficiency and energy saving of the whole process. The efficient recycling of ionic liquids and the valorization of the lignin byproducts can also promote the large-scale utilization of ionic liquid pretreatment processes. Ionic liquids are not necessarily pure, which also increases the difficulty of recovery to a certain extent.
2. To increase the commercial value of the fractionation process, the lignin and hemicellulosic fractions could be considered as the high-valued bioproducts. However, both fractions containing a wide variety of degradation products, including oligomers, monomers, and derivatives, make this process more challenging. Although certain ionic liquids can dissolve all the components of lignocellulosic biomass, it is not easy to obtain pure fractions.

Table 3
The common types of the cations and anions of ionic liquids.

Types of cations	Types of anions
Tetraalkylammonium ($R1R2R3R4N^+$)	Halogen salt: Cl^-, Br^-, I^-, Br_3^- …
1,2,3-Trialkylimidazolium ($R1R2R3Im^+$)	Alkali salt: OH^-, CO_3^{2-}、HCO_3^-…
Alkylpyridinium ($R1Py^+$)	Fluorine-containing anions: $BF4^-$, $PF6^-$, FSI^-, $TFSI^-$, $SbF6^-$, TfS^-
Dialkylpyrrolidinium ($R1R2Pyr^+$)	Organic oxygen-containing acid: Ac^-, MS^-
Dialkylpiperidinium ($R1R2Pip^+$)	Amino acid: Lac^-, Cys^-, Gly^-
Tetraalkylphosphenium ($R1R2R3R4P^+$)	Ester: SO^-, SDd^-, SHd^-, PB^{2-}
Trialkylsulfonium ($R1R2R3S^+$)	Halide: $FeCl_4^-$, $AlCl_4^-$, $ZnCl_2^-$, $CuCl_2^-$

3. Compared to the conventional solvent, the price of ionic liquids is more expensive, which limit its commercial application at large scale fractionation plants. How to reduce the synthesis cost of ionic liquids by using inexpensive raw materials is essential.

4. Some ionic liquids or their derivatives can be toxic which can cause an irreversible inactivation of enzymes in subsequent conversion processes. The ionic liquids solution could become viscous after cellulose extraction. This undoubtedly increases the difficulty of recycling hemicelluloses and lignin.

Based on the concept of biorefinery, the recovery of chemicals and products is an integrated process which involves the recovery of ionic liquids, lignin and hemicelluloses, as well as the removal of water. The complete demonstration of a fairly simple and low-cost regeneration process of the chemicals in solution should be built to produce clear ionic liquids, lignin and hemicellulosic fractions. Developing an efficient recycling and reuse technique is more favourable than the reduction of the synthesis cost of ionic liquids to overcome the limitation of commercial operation for the fractionation of biomass. The combination of the ionic liquid fractionation with other assisting method, such as microwave and ultrasound, can be considered to be an integrated process to overcome the economical and technological issues of single treatment. Future work should also more focus on rheological properties of ionic liquid mixture in order to fulfill this knowledge gap. Furthermore, the applications of biobased ionic liquids which are synthesized from biobased compounds are expected to improve the environmental sustainability of ionic liquid fractionation.

5. Deep eutectic solvents (DESs) fractionation

5.1. Current progress of DESs fractionation for lignocellulosic biomass

Deep eutectic solvents (DESs) are used as a new kind of green solvent, with the advantages including the simple preparation process, biodegradability and biocompatibility. DESs own great application potentials in the fields of electrochemistry, organic synthesis and biocatalysts. Especially, DESs have shown good application prospect in the biomass refining and lignocellulosic biomass fractionation. Francisco et al. (2012) reported the DESs composed of organic salts and natural carboxylic acids for the first time in 2012, which exhibit good dissolution capacity towards the original wheat straw. Since then, the research of DES has been carried out and most of the studies have achieved satisfactory results.

The eutectic solvent is a mixture consisting of hydrogen bond donor (HBD) and hydrogen bonding acceptor (HBA), including a variety of anionic and cationic substance. The composition can be expressed by general formula of $Cat^{+}X^{-}_{z}Y$, in which Cat^{+} stands for the ammonium salt, phosphorus salt and sulfonium cation; X^{-} stands for a Lewis base, which is mostly a Halogen anion and can form complex anion with hydrogen bond donor (Y); and Z is the number of molecules of Y. DESs

are soluble with water and easily to prepare, owning numerous advantages including low volatility, non-combustibility, good biocompatibility, biodegradability, recyclability and cost effectiveness. Most of the DESs are molten salts, and the hydrogen bonds formed by HBD and HBA could reduce the entropy difference of phase transition and weaken the crystallization ability of the original material (Francisco, 2013).

Commonly, DESs can be divided into 4 types according to the chemical constituents as shown in Fig. 3. Among these, Type III DESs are the most popular depended on their quick and easy preparation, biodegradability, non-reactivity with water and low-cost. Type II DESs are also relatively viable for the industrial productions due to the relatively low costs of the hydrated metal halides. The application of Type I is limited because of its high melting points of the non-hydrated metal halides. Type IV EDSs incorporate the inorganic transition metals and urea, although the metal salts would not ionize normally in the non-aqueous media.

In general, the physicochemical properties of DESs and ionic liquids are similar. Moreover, the halogen anions in DESs and lignin can form hydrogen bonds, and selectively break the ether bond between the structural units of phenylpropane in lignin, so as to dissolve the lignin and hemicelluloses during biomass fractionation process (Loow et al., 2018). The remaining solid component of the lignocellulosic biomass processed by DESs is mainly composed of cellulose with high crystallinity. As shown in Table 4, the operating conditions of fractionation process, including treatment temperature, time and solvent viscosity, would directly affect the treatment performance of DES. The reaction temperature usually exceeds 100 ºC, and the higher temperature could contribute to shorten the reaction time and increase the obtained fraction yield. The DES fractionation process is universal and could be used to a variety of lignocellulosic biomass. Furthermore, DESs fractionation consumes less energy compared with the other traditional pretreatment methods. Short-time and high efficiency are decisive factors concerning the application performance in industrial scale. The assisting technologies are commonly combined with the DESs fractionation to enhance the reaction efficiency, including the microwave technology, ultrasonic technology, hydrothermal method, and inorganic salt pretreatment, etc. (Chen and Wan, 2018; Loow et al., 2018; Ma et al., 2019; Shen et al., 2021). Thus the reaction time could be shorten due to the combined technologies could greatly destroy the cell wall of lignocellulosic biomass (Carrión-Prieto et al., 2018; Gawade and Yadav, 2018). It has been demonstrated that DES could be used as an efficient liquid to isolate the lignin from lignocellulosic biomass via a one-pot step (Malaeke et al., 2018). The lignin with a high purity and highly retained cellulose from corncobs were achieved by DES fractionation with a short-time treatment (Guo et al., 2019b). The DES fractionation of sago waste could yield 5.2 mg/mL of glucose with a low reducing sugar loss (Wan et al., 2018). Moreover, the selective removing of lignin and hemicelluloses in turn could increase the subsequent enzymatic hydrolysis of the residue cellulose (Song et al., 2019). It is reported that the environmentally friendly heteropoly acids were used as catalyst to
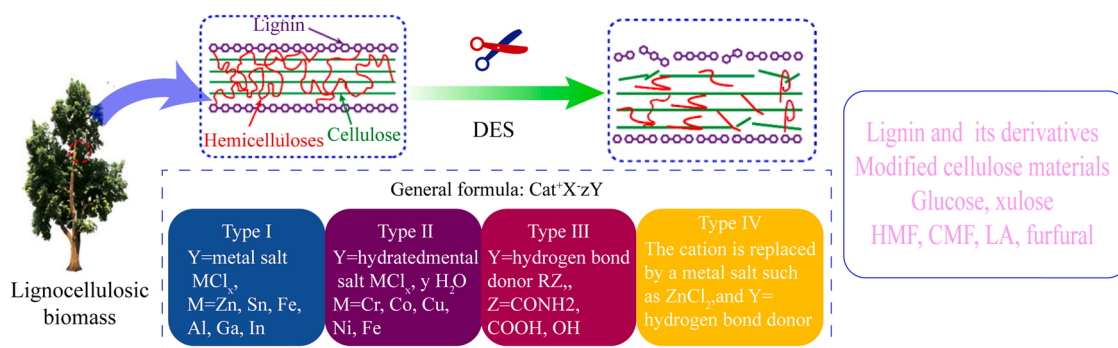

Fig. 3. DES classification and the fractionation process of lignocellulose biomass.

Table 4
DES fractionation processes.

Fractionation reagent	Raw material	Fractionation conditions (T: temperature; t: time; L/S: liquid/solid ratio)	Main outcome	Ref.
ChCl:urea (1:2)	Oil palm	T:60–140 °C; t: 2–10 h; L/S: 10/1	Hemicellulose removal: 74%	(Loow et al., 2018)
ChCl: lactic acid (1:2)	Corn stover	T: 152 °C; t: 45 s; L/S: 10/1	Hemicellulose removal: 90.06; Lignin removal: 79.60%; Cellulose-to-glucose conversion yield: 78.5% after enzymatic hydrolysis	(Chen and Wan, 2018)
ChCl: glycerol (1:2)	Miscanthus	T: 120 °C; t: 3 h; L/S: 20/1	Hemicellulose removal: 58.5%; Lignin removal: 89.5%; Cellulose-to-glucose: 97.3%	(Guo et al., 2019a)
benzyltrimethylammonium chloride: lactic acid(1:2)	Cormcobs	T: 100–140 °C; t: 2 h; L/S: 20/1	Hemicellulose removal: 80.8%; Lignin removal: 63.4%; Cellulose-to-glucose: 96.9%	(Guo et al., 2019b)
betaine: lactic acid (1:2)	willow chips	T: 50–140 °C; t: 3 h; L/S: 20/1	Lignin removal: 96%	(Song et al., 2019)
ChCl: formic acid (1:2)	Cormcobs	T: 90 °C; t: 9 h; L/S: 25/1	Lignin removal: 69.52%	(Li et al., 2021)

improve the treatment performance of neutral DES (choline chloride/glycerol). The results showed that 81.8% of ethanol yield and 80% of glucose yield were achieved, accompanied with the significant delignification as high as 89.5% (Guo et al., 2019a).

5.2. Current challenges and future prospects of DES system for biomass fractionation

As a novel dissolving system of lignocellulose resources, the appearance of deep eutectic solvents brings opportunities for realizing the full utilization of lignocellulose resources. However, great challenges are still existing in the present. The delignification with a high efficiency needs a relatively high operation temperature, since the low viscosities of DESs would positively promotes the delignification of the biomass which enhances the mass transfer of the system. Thus, the high acidity for the specific HBD (oxalic acid), pulp charring and release of CO_2 at high temperatures would limit the scale-up production. The higher temperature also poses a negative effect on recovering the sugar (Procentese et al., 2015), leads to the lignin structural variation (150 °C) and reduces the lignin yield due to the attachment on the residual solid (Lou et al., 2019). The hydrogen bonding between the HBA and HBD is related with the capability of proton (H^+) to detach from DES which influences the efficiency of hemicelluloses removal and delignification. The addition of water could increase the viscosity of DES, which is helpful for the considerable reduction in hydrogen bonding interactions and thus decrease the viscosity. Recently, the most widely used precursor-choline chloride that has been used as the food additive, combined with the natural and cost-effective HBD (glycerol, carboxylic acid or urea) to form the natural deep eutectic solvents (NADESs) which are biodegradable. However, most of the DESs are hydrophilic or moisture sensitive which would increase the drying and transport expenses. In this regard, the hydrophobic DESs should be developed urgently to overcome this disadvantage.

Further modifications should be constructed and related with the appropriate procedures for the DES pretreatment of biomass materials which is related with the removal of H^+ from the HBD and helps break the -O- (ether) or -CO-O-C- (ester) bonds of the lignin-hemicelluloses material. Numerous studies have shown the factors that greatly influenced the overall dissolution process including the type of alkyl chain length, ammonium cation and the presence of pH end-group. Specifically, the alkyl chain of longer lengths could reduce the interactions between the cation centers and the anions. Commonly, to further improve the delignification efficiency, some assisting methods including the chemical additions (dilute acid or alkaline treatment) or physical methods (microwave irradiation, ultrasonication) are adopted to improve the reaction area, response efficiency and decrease the energy. In view of this fact that the physicochemical properties of DES are greatly related with the modulation of species and behavior of DES,

future advances should exist in the in-depth design in formulating a targeted DES. Apart from that, developing thermal stable and recyclable DES is essential and greatly needed, since the reutilization of DES solvents could interfere the interactions between HBAs and HBDs, due to their high thermal instability as well as susceptibility to contaminants.

6. Conclusions

Lignocellulosic biomass is a renewable resource due to its numerous advantages including biodegradability, renewability and broad sources, etc. However, the complex structure of lignocellulose and its recalcitrance limit its wide application. Therefore, we need to set about from the following aspects: firstly, in order to realize a green and low-cost separation, new low-cost and efficient separation approaches have to be developed and realized in the lignocellulosic fraction research, such as the high temperature assisted liquid water method and deep eutectic solvent method. The ideal separation method of green, environmental protection and low-energy consumption is the aim we hope to achieve, which is also the trend of biomass component separation research. The methods mentioned in this article including the high-temperature assisted liquid water method and deep eutectic solvent method are closely related with the ideal standard at present, but needs further scale-up pilot tests to realize the industrial operation use. In addition, the separation of biomass components can be coupled with the subsequent utilization process, which can not only reduce the corresponding energy consumption, but also make full use of the three components of biomass to achieve the biomass refining.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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