Editorial Corner

Recent Trends and Updates for Chemical Pretreatment of Lignocellulosic Biomass

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Global economic growth over the past decades has depended abundantly on fossil fuels and their limited reserves. The steady depletion of fossil fuels has been a constant concern for researchers and industries these days. The excessive use of crude oil and derived products leads to environmental problems such as (a) greenhouse gas (GHG) emissions, (b) climate problems and (c) air pollution. During the 26th UN Climate Conference (COP26) held in Scotland in 2021, the problems related to climate changes and GHG emissions were discussed. Emission of GHG has negatively affected the climate all over the world. For the current rate of GHG emission, obtaining an average temperature rise greater than 1.5 °C due to global warming is possible. Therefore, countries should start working towards achieving one goal set by COP26 "*Secure global net zero by mid-century and keep 1.5 degrees within reach*" [1]. To achieve the goal, researchers in different countries have been encouraged to study energy derived from renewable resources. In recent years, researchers are prompted to look for the alternative renewable source to produce biofuels, biogas, chemicals, platform chemicals and value-added products [2]–[4]. Lignocellulose (plant material) is the most common promising renewable source that can be utilized for the production of chemicals and other valuable by-products. The content of the lignocellulosic biomass includes two polysaccharide layers (hemicellulose and cellulose) and one polyaromatic layer (lignin). The sugars present in the cellulose and hemicellulose layer can be converted to fermentable sugars by pretreatment and enzymatic saccharification [5].

On the other hand, lignin (complex matrix) serves as a protective layer (like a bubble wrap) for hemicellulose and cellulose from degradation. Due to the complex structure of lignin, lignocellulosic biomass is recalcitrant towards enzymatic hydrolysis and microbial degradation. Thus, pretreatment is considered as an essential step to overcome the recalcitrant property of lignocellulose and achieve a high sugar yield during enzymatic saccharification. Cleavage of the linkages, hydrogen bonds, solubilization of hemicellulose, and reducing the cellulose crystallinity through different pretreatment techniques has been the primary focus of researchers for several decades. To facilitate the production of bioethanol and other chemical by-products during fermentation, the pretreatment of lignocellulose mainly aims to remove lignin and hemicellulose by keeping the cellulose in the solid phase for further steps, such as saccharification and fermentation [6].

Acid, alkali, ionic liquid, deep eutectic solvents, organosolv, methods are classified under chemical pretreatment. In acid pretreatment, lignocellulosic biomass is fractionated using acids (either diluted or concentrated) [7]. On the basis of concentration, the action of acid on lignocellulosic biomass results in the destruction of β-(1→4) glycosidic bonds, solubilization of hemicellulose and cellulose, and lower lignin modification. However, an increase in acid concentration and reaction times, results in further degradation of the solubilized sugars to inhibitory compounds (furfural and 5-hydroxymethylfurfural) and instruments corrosion. The inhibitory compounds can subsequently decrease

the saccharification and fermentation efficiency [8]. Therefore, finding an optimal condition is an essential step during pretreatment of different lignocellulosic biomass. Some conventional acids that have been studied are sulphuric acid, hydrochloric acid, phosphoric acid, and acetic acid. However, in recent years, organic acids (oxalic acid, maleic acid, citric acid) have been preferred due to the lower yield of inhibitory compounds [9], [10]. Meanwhile, alkali pretreatment involves the solubilization of the recalcitrant layer (lignin) and hemicellulose. The pretreatment is usually performed for a period of time (10–90 min or several hrs) with alkali concentration and temperatures varied as 1–7 %wt and 50–200 °C, respectively. In addition, the crystallinity of the cellulose decreases resulting in increase of the crystallinity index (CrI). Furthermore, solubilized lignin is precipitated by lowering the pH (2.0) of the black liquor obtained after alkali pretreatment. Subsequently, the saccharification process is enhanced and a high sugar yield is achieved. However, drawbacks of alkali pretreatment include the generation of wastewater and salt formation during pH neutralization [11].

On the other hand, ionic liquid pretreatment overcomes the drawback of acid and alkali pretreatment. Ionic liquids are molten salts under room temperature with anion and cations. Among different anions and cations, imidazolium, pyridinium, choline and chloride, acetate are the most common selected species, respectively [12]. During pretreatment, the β-O-4 bonds are converted to ion dipole bond. However, the pretreatment efficiency depends extensively on the selection of cations and anions. Ionic liquid pretreatment dissolutes the cellulose layer resulting in the separation of hemicellulose and lignin. The solubilized cellulose can be regenerated (reduced crystallinity) by additions of anti-solvents (water or alcohol). The regenerated celluloses with different crystalline properties are more susceptible to enzyme action resulting in high sugar yields [13]. Though, ionic liquid offers such advantages, ionic liquids are expensive, and the residual ionic liquids in biomass after pretreatment can inhibit the enzyme and microorganism metabolism [14]. [15]. Therefore, the drawback of ionic liquid pretreatment is overcome by deep eutectic solvents. Deep eutectic solvents (DES) with similar properties to ionic liquids are new generation green solvents. These solvents are cost effective, ease at preparation and are non-toxic to microorganisms. The green DES solvents compose of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) at different molar ratios. During pretreatment, a new hydrogen bond is formed between the hydroxyl groups (lignin) and carbohydrates resulting in the hydrolysis of the lignin carbohydrate complex (LCC) bond due to the interaction of HBD/HBA and the formation of acid-alkali catalytic solution that results in cleavage of the ether bonds between lignin and hemicellulose [16]. However, the pretreatment efficiency is dependent on the selection of the HBD and HBA. The solubilized lignin can be recovered through precipitation using acetone/water mixture. Organosolv pretreatment cleaves the β-O-aryl, α-O-aryl, and 4-O-methylglucuronic acid ester bonds between hemicellulose and lignin. Methanol, ethylene glycol, ethanol, and acetone are some of the most common solvents used [17]. The pretreatment is performed with a temperature range of 150–220 °C. In recent years, a combination of two solvents and their effects on lignin and hemicellulose solubilization are being studied extensively.

In recent years, multi-step pretreatment is being studied (combining two pretreatment methods at the different stage). Combining methods provide more opportunity by recovering of the products at different stages [18]. Such a strategy contributes to the production cost of biofuel. Further multi-step pretreatment also requires low energy and harsh chemicals, which enhances the saccharification and fermentation process. For instance, using low concentration acid and alkali at two different steps results in low sugar degradation, instrument corrosion, and wastewater generation. Furthermore, combining hot water and deep eutectic solvent pretreatment results in the removal of hemicellulose and lignin at different stages. The combination of hot water with other chemical methods has been studied extensively. This is due to (a) the lower effect of hot water on cellulose structure, (b) modification of lignin structure, and (c) hemicellulose solubilization [19]. This approach can overcome the limitations of single stage pretreatment. Furthermore, biorefineries with this approach could lead to the production of biofuels or bio-products that could be a good alternative to existing fossil products in the industry. However, optimization of such approach is required with application to multiple lignocellulosic biomass.

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