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Comparison of Chemical Pretreatment Methods for Cellulosic Biomass

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Abstract

The variety in physiochemical characteristics of cellulosic biomass reveals the need for pretreatment technologies to help in the rapid and efficient conversion of carbohydrate polymers into fermentable sugars. Suitable pretreatment methods enhance the enzymatic hydrolysis of biomass because of the crystalline structure of cellulose and the complex structure of lignin and hemicellulose. The choice of pretreatment method affects on the sugar yield, avoids the degradation of sugars derived from hemicellulose and minimize the formation of inhibitors for subsequent fermentation steps. A suitable process should minimize heat and power requirements to be cost effective in operation. The present review focuses on various chemical pretreatment methods for lignocellulosic biomass based on recent reports in literature. An analysis of the methods shows that the composition of biomass is the main factor in the selection of pretreatment method.

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Keywords: cellulosic biomass, cellulose, pretreatment, lignocellulosic, lignin, hemicellulose, enzymatic hydrolysis

1. Introduction

Lignocellulose biomass is a complex that mainly consists of cellulose, hemicellulose, and lignin [1]. The composition of these compounds directly depends on their source, whether hardwood, softwood, or grass. Cellulose with a particular crystalline structure that is insoluble in water is resistant to depolymerization.

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Hemicellulose, which provides structural backbone to plant cell wall, is a branched polymer of glucose or xylose. According to literature [2], cellulose and hemicellulose are probable sources of fermentable sugars. These sugars are first produced after a pretreatment process of cellulose polymer, followed by enzymatic hydrolysis. Lignin provides further strength to plant cell walls, but hinders the enzymatic hydrolysis of carbohydrates. Several chemical pretreatment approaches have been developed to remove hemicellulose and lignin and decrease the crystallinity of cellulose to enhance the biodegradability of cellulose and sugar yield in enzymatic hydrolysis to maximize the volumetric productivity of the cellulosic feedstock. Highly digestible solids that enhance sugar yields while avoiding the degradation of sugars and minimizing the formation of inhibitors for the subsequent fermentation steps are produced during the treatment process. These technologies are cost effective, with minimum heat and power requirements; they are also environment friendly [3]. This study aims to review promising chemical pretreatment methods with emphasis on suitable feedstock these methods are used for and the merits and disadvantages of each method. This paper shows the importance of the pretreatment process for the subsequent enzymatic hydrolysis and conversion of cellulosic feedstock to valuable products in fermentation. Fig. 1 represents the pretreatment steps that finally lead to the generation of sugars as substrates for biofuel production.

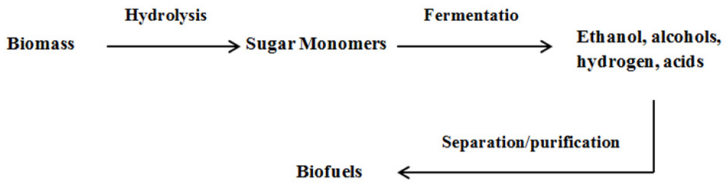

Fig 1. Schematic of the conversion of lignocellulosic biomass to fuel (4)

2. Acidic Pretreatment

Acid pretreatment usually involves the addition of concentrated or diluted acids of 0.2 w/w% to 2.5 w/w% to the biomass, and continually mixing at 130 °C to 210 °C. Dilute acid hydrolysis is performed in two different conditions, namely, high temperature (T > 160 °C) in continuous mode for low solid loading and lower temperature (T ≤ 160 °C) in batch mode for high solid loading [5]. In strong acid hydrolysis, concentrated strong acids such as H_2SO_4 and HCl are used without subsequent enzymatic hydrolysis. This reaction is carried out in mild temperature conditions with different types of feedstock and high sugar yield [6]. In dilute acid hydrolysis, the firm structure of the lignocellulosic materials is cracked, followed by the removal of hemicelluloses, which increases the porosity and enzymatic digestibility of biomass [7]. Organic salts can also be used in dilute acid treatment [8]. The key advantage of this method is the high solubility of hemicellulose and lignin in acid, with high yield of glucose without need for subsequent enzymatic hydrolysis [9]. However, the recovery of acids used in this process is expensive and corrosion-resistant equipment is costly [10]. In addition, inhibitors of fermentation such as hydroxyl methyl furfural are produced in high concentration, thereby reducing the effectiveness of this method [11]. The method is suitable for biomass with low lignin content because lignin is not removed from the biomass. Moreover, the optimal condition of the acid pretreatment is extremely important.

3. Alkaline Pretreatment

In this method, biomass is soaked in alkaline solutions, such as calcium, potassium, sodium and ammonium hydroxide and then mixed at a suitable temperature for a certain amount of time. This process

involves alteration in the structure of lignin, partial decrystalization of cellulose and partial solvation of hemicellulose [12]. Lignin is separated from inhibitors through neutralization. Alkaline process requires less severe conditions compared with the other pretreatment methods. The results of the alkali pretreatment on corn stover, switchgrass, bagasse, wheat, rice straw, hardwood, and softwood have revealed the effectiveness of this method. In lime pretreatment, CO_2 was used for neutralization without the need for solid–liquid separation step. However, lime pretreatment is cost effective and energy intensive compared with other alkaline pretreatment methods. The recovery of $CaCO_3$ has been successfully performed through precipitation with CO_2 [13]. In some studies, alkaline pretreatment has been combined with other pretreatment methods to efficiently treat high-solid content biomass [14]. In this method, lignin is effectively removed and its structure is altered. This method is applicable to various biomasses and potential of sugar yield is high. This method has been proven in pilot although operational cost is high [6]. The catalysts suitable for alkaline pretreatment are expensive and lower amounts of inhibitors are formed in this process.

4. Wet Oxidation

Wet oxidation pretreatment is performed at 195 °C for 10 min to 20 min and begins with drying and milling of lignocellulosic biomass. The process continues with the addition of water and Na_2CO_3 to reduce the fermentation byproducts. Afterward, air is introduced into the system to oxidize the compounds dissolved in water [15]. The advantage of this method is that hemicellulose is solubilized, lignin is removed, and lignocellulosic materials are fractionated [16]. The combination of wet oxidation with chemical and physiochemical methods increased the yield of sugar [17]. This pretreatment process is efficient for a variety of agricultural wastes including wheat straw, corn stover, sugarcane bagasse, cassava, and canola, although the potential yield of sugar is not high and this method has not yet been proven in the pilot [6].

5. Ionic Liquids

Ionic liquids can dissolve a variety of biomass with different hardness [18], and are introduced as selective solvents of lignin and cellulose. In this process, biomass is solubilized in the solvent at 90 °C to 130 °C and ambient pressure, followed by the addition of water to precipitate the biomass. The process is completed by washing the precipitate. The structure of lignin and hemicellulose are unaltered after treatment with ionic liquids, allowing the selective extraction of unaltered lignin [19] because lignin is highly soluble in solvents while cellulose shows low solubility. This occurrence can result in the separation of lignin and the enhancement in cellulose accessibility under ambient temperature and pressure without alkaline or acidic reagents and inhibitor compound formation. These solvents are expensive; however, the cost of their recovery is not high because of the low vapor pressure of the solvents. Nevertheless, cellulase enzyme is irreversibly inactivated in ionic liquid solvents [20], which lowers biomass conversion efficiency and increases the overall cost. This result shows the need to develop solvents in which cellulase and microorganisms are active.

6. Oxidative Delignification

Oxidative delignification involves treatment of biomass with oxidizing agents, such as ozone, hydrogen peroxide, or oxygen. Oxidizing agents with aromatic rings convert lignin polymer into carboxylic acids, which are inhibitors of microorganisms. However, part of the hemicellulose fraction of biomass may be degraded. In ozonolysis, degradation is limited to lignin, whereas hemicellulose and cellulose are not degraded [21].

The rate of enzymatic hydrolysis of ozone-treated biomass is increased because of lignin removal through

pretreatment. Ozonolysis oxidations are more effectively conducted in hydrated fixed bed than in aqueous suspension. These experiments are conducted at room temperature and ambient pressure. Ozone is expensive; however, it can be easily decomposed and can minimize environmental pollution.

7. Organosolv

In this method, organic solvents such as ethanol, methanol, acetone, and ethylene glycol or their mixture with water are used to remove lignin and hydrolyze hemicellulose, leading to the improved enzymatic degradability of cellulose [22]. However, solvents should be removed before fermentation, which is a costly process. The temperature of the process is about 200 °C or less, depending on the type of biomass and catalyst. High-quality lignin is produced in organosolv pretreatment, which can be used for production of chemicals. The removal of lignin decreases the cost of enzyme because the absorption of cellulase to lignin is decreased. In this method formation of inhibitors of fermentation is very low although this method is applicable to various biomasses with a high potential of sugar yield [6].

8. Conclusion

The chemical pretreatment processes were compared based on their brief descriptions, followed by the advantages and disadvantages of each process. Process complexity and reliability differ; consequently, their potential for creating higher sugar yields are different in such a way that introducing the best pretreatment method is not possible. These processes focus on lignin removal and in enhancing the enzymatic degradability of cellulose. Acid pretreatment particularly enhances the hydrolysis of hemicellulose to sugars. For the limitations considered for each chemical method, any treatment that requires lower-cost chemical reagents and conditions and yields more sugar is preferable.

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