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Commentry

Development of Pretreatment of Lignocellulose for Bioenergy

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ABSTRACT

The overuse of fossil fuels causes serious shortages problems and environmental issues. Lignocellulosic material is an abundant, inexpensive and carbon-neutral renewable bio resource for the production of biofuel and bio-based products. In this commentary, the researches of various pretreatments for enhancing the enzymatic digestions of lignocellulosic materials are introduced. The pretreatment process and its synergistic effects on enzymatic digestion of lignocellulosic materials are discussed. These studies showed that combination of effective pretreatments is a promising strategy for improving enzymatic hydrolysis of biomass.

Keywords: Lignocellulose; Pretreatment; Bioenergy; Saccharification

INTRODUCTION

Lignocellulose mainly consists of cellulose, hemicellulose and lignin, along with small quantities s of proteins, pectins, extractives, and ashes [1]. The typical process for converting biomass into biofuel and bio based chemicals is mainly composed of three steps: biomass pretreatment, enzymatic hydrolysis, and fermentation [2]. The hemicellulose and cellulose are usually densely packed together with lignin, which result in low enzymatic saccharification [3]. An ideal biomass pretreatment process is capable of disrupting recalcitrant lignocellulosic structures, removing lignin to expose the cellulose and hemicellulose, increasing the enzyme accessibility to cellulose and hemicellulose, and enhancing the yield of fermentable sugars [4]. Various pretreatments have been attempted to pretreat lignocellulosic materials for enhancing the reactivity of cellulose molecules with cellulases and improving the enzymatic saccharification [5]. During the pretreatment of biomass, the removal of hemicellulose and lignin depends on the pretreatment technology, operation conditions, and pretreatment severity. Generally, the depolymerization of lignin and polysaccharides intimately associates with each other result in the effective utilization of lignocellulosic material. The pretreatments include physical (milling, chipping, and grinding), chemical (concentrated alkali, concentrated alkali, dilute alkali, dilute acid, oxidizing agents, and organic solvents), physicochemical (steam pretreatment/autohydrolysis, hydrothermolysis, and wet oxidation), biological, or their combination [6].

CHEMICAL PRETREATMENT

Ozonolysis

In biomass, lignin's association with cellulose protects it from enzymatic hydrolysis. Ozone (O_3) pretreatment can be used to degrade lignin and remove hemicellulose in lignocellulosic materials. Ozone pretreatment can be used to reduce lignin content significantly. However, hemicellulose in biomass can be removed slightly. Ozone pretreatment can becarried out at room temperature under normal pressure [7]. A disadvantage of ozone pretreatment is that a large quantity of O_3 is required, which restrict its application due to its high economic cost [8].

Acid pretreatment

Inorganic acids are known as common catalysts for the biomass pretreatment [9]. Concentrated acid pretreatment allows to obtain high yield of reducing sugars from biomass at low temperature [10]. Acid hydrolysis rate of crystalline cellulose is slower than that of amorphous hemicellulose in biomass due to their different intrinsic properties. After acid hydrolysis is carried out by concentrated acid in one step, pentoses and hexoses from hemicellulose in biomass are more susceptible for degrading into furfural and 5-hydroxymethylfurfural (5-HMF), which can inhibit the subsequent fermentation of reducing sugars. Additionally, concentrated acid pretreatment has the disadvantages including high consumption of acid, corrosion of the equipment, toxicity to the environment, andenergy consumption for acid recovery. Compared to concentrated acid pretreatment, dilute acid pretreatment has the merit of lower acid consumption.

Alkaline pretreatment

In biorefinery, alkaline pretreatment (AP) is essentially employed for the reduction in the degree of polymerization and crystallinity, swelling of the fibers, as well as disruption of the lignin structure removing lignin in biomass, which improves the enzymatic accessibility of the polysaccharides [11]. Alkaline pretreatment

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of biomass originates from soda pulping. NaOH, KOH, NH_3, $Ca(OH)_2$, and oxidative alkali have been developed as main alkali agents for biomass pretreatments [12]. Alkaline pretreatment can be performed at lower temperature under the normal pressure, resulting in a higher sugar recovery than acid pretreatment.

PHYSICAL PRETREATMENT

Mechanical pretreatment

Chipping, grinding, and milling are common mechanical pretreatment processes. The main intention of mechanical pretreatment is to disintegrate the solid particles of biomass, subsequently releasing biomass fragments with small particle size and permeability inside the overall lignocellulosic biomass structure. To decrease the crystallinity of cellulose in biomass and enhance its saccharification, vibratory ball milling was found to be more cost-effective than ordinary ball milling (OBM). Grinding and milling can effectively reduce the particle size and cellulose crystallinity because of the shear forces generated during milling, while chipping can significantly reduce the limitations of mass and heat transfer [13].

Pyrolysis

Pyrolysis, a thermal degradation process, has been employed for pretreating lignocellulosic materials in biorefinery processes. Pyrolysis pretreatment is divided into slow, intermediate, fast, and flash pyrolysis based on the required heating rate and residence time [14]. In addition, it is flexible in production and marketing. Pyrolysis is known as a thermal decomposition process, occurring in the absence of oxygen, which can convert lignocellulosic materials into carbon-rich solids and liquids. Pyrolysis is found to be more efficient when performed in the presence of oxygen at lower temperatures.

Irradiation

Recently, various radiation pretreatments under ultrasonic, electron beam, UV, and microwave heating have been employed to pretreat lignocellulosic biomass for enhancing its saccharification [15]. Microwave irradiation is widely employed for biomass pretreatment due to its simplicity, low energy consumption, high heating capacity in short-duration time, and minimum generation of fermentation inhibitors [13]. Ultrasound waves can alter the morphology of lignocellulosic materials. Ultrasound with frequency of 10–100 kHz for biomass pretreatment can be effective for cell breakage and polymer degradation [16]. Based on the biomass and slurry characteristics, power and duration of sonication need be optimized to meet the desired pretreatment objectives.

PHYSICAL-CHEMICAL PRETREATMENT

Steam explosion

Steam explosion pretreatment, a typical combination of mechanical forces and chemical effects, is one of the most commonly used methods for pretreating lignocellulosic materials. Lignocellulosic materials are subjected to high pressure saturated steam at the temperatures of 160–260°C and the pressure of 0.7–4.8 MPa for given pretreatment time, resulting in the hydrolysis and release of hemicellulose [13]. The steam enters the lignocellulosic biomass expanding the cell walls of fibers leading to partial hydrolysis and increasing the cellulose accessibility to cellulases [17]. The main factors that affect steam explosion pretreatment are residence time, pretreatment temperature, chip size, and moisture content. Lower pretreatment temperature and longer residence time are more favorable [18].

Liquid hot water pretreatment

Liquid Hot Water (LHW) is known as one of the most promising pretreatment methods due to the advantages of no additive chemicals requirement, which is alsotermed aqueous fractionation, aquasolve, solvolysis, hydrothermolysis, and hydrothermal pretreatment [19]. Although LHW can be conducted at low temperature with low cost of the solvent, a large quantity of water is required to be recovered in downstream processing [20].

BIOLOGICAL PRETREATMENT

It is known that hemicelluloses, lignin, and polyphenols can be utilized by biological pretreatment (BP) involving the action of bacteria and fungi with high substrate specificity, low energy cost, and no generation of toxic chemicals [21]. Fungi are highly efficient degradation candidates of biomass and play an essential role in the global carbon cycle and ecology [22]. Fungal pretreatment has been used as an effective way for enhancing enzymatic saccharification of lignocellulosic biomass for producing biofuel or bio based products [23]. White-rot and brown-rot fungi are known to be good candidates for pretreating biomass.

SUMMARY

Finally, we have a overview of effects of pretreatments on lignocellulose. The effects of several pretreatments on the physical/chemical composition or structure of lignocellulose is shown in Table 1, which summarizes the most popular different pretreatment methods discussed in this paper. It suggests that increasing the surface area is one of the major approaches of a pretreatment by solubilization of the hemicellulose and/or lignin.

Table 1: Effects of the different pretreatments on the physical/chemical composition or structure of lignocellulose.

Treatments	Increase accessible surface area	Decrystallization cellulose	Solubilization hemicellulose	Solubilization lignin	Formation furfural/ HMF	Alteration lignin structure
Ozonolysis	+	+	+	+/-	-	+
Acid Pretreatment	+	+	+	-	+	+
Alkaline Pretreatment	+	+	+	-	+	-
Mechanical Pretreatment	+	+	ND	ND	-	-
Pyrolysis	+	ND	ND	ND	+	+
Irradiation	-	ND	ND	ND	-	+
Steam Explosion	+	+	+	-	+	+
Liquid Hot Water Pretreatment	+	+	+	-	-	-
Biological Pretreatment	+	+	+	+	-	+

Note: +: Major effect; -: Minor effect; ND: Not determined.

Many kinds of lignocellulosic biomass have been used as cheaper starting materials for the production of biofuels. One pretreatment technology to help in the rapid and efficient for one type of lignocellulosic material might be not suitable for pretreating another material. The major advantages and disadvantages of these common technologies for pretreating lignocellulosic materials are summarized. The choice of the pretreatment technology to help in effective conversion of a particular lignocellulosic biomass depends on its composition and the by-products produced as a result of pretreatment. These factors significantly affect the costs associated with a pretreatment method. There have been some reports comparing various pretreatment methods for biomass. Cost-effective pretreatments for enhancing the enzymatic saccharification deserve in-depth investigation.

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