TECHNOLOGIES FOR LIGNOCELLULOSE PRETREATMENT TO PRODUCE FUEL ETHANOL

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Abstract. Bioethanol is one of the alternatives to fossil fuels. Bioethanol production from lignocellulose has advantages on source richness, but it has poor performance on the conversion yield. In order to destroy the structure of lignocellulose and promote the cellulose and other components release, lignocellulose treatment was necessarily prior to bioethanol fermentation. In this paper, eight methods for lignocellulose pretreatment were reviewed including physical method, dilute acid pretreatment method, dilute alkali pretreatment method, steam pretreatment method, ammonia pretreatment methods, organic solvent pretreatment method, ionic liquid pretreatment method and biological pretreatment, and those principles and novel progresses were briefly introduced.

1. Introduction

The excessive consumption of fossil fuels has brought about energy crisis as well as a large number of environmental problems. Developing new energy is an effective way to reduce environmental pollution and alleviate energy shortage. Among the diverse new energies, biomass energy has been widely concerned because it is a source-extensive, reserve-abundant, renewable and environment-friendly energy source (Karakashev et al., 2007).

Biomass can produce fuel ethanol by fermentation. As one category of fuel, fuel ethanol is one of the most ideal substitutes for petroleum because it has the features of low pollution, strong anti-explosion and it can release high calorific value when it was burnt. The research octane number of ethanol is 108 which is higher than that of gasoline, so the addition of ethanol to gasoline can improve the antiknock property of gasoline. As a gasoline additive, ethanol causes lower adverse effects on environment and humans compared with methyl tert-butyl ether (MTBE). Although the calorific value of ethanol is lower than that of gasoline, the thermal efficiency of the engine can be improved by increasing the compression ratio (Zhao T.T. et al., 2015; Ye W.G., et al., 2018).

There are many kinds of biomass raw materials can be utilized to produce ethanol. Starch and sugar could be considered as the first-generation sources to produce ethanol, and ethanol production from these raw materials by microbial anaerobic fermentation had been widely investigated and used in the industry. However, the starch and sugar are also one of the main food sources for humans, the usage of them on ethanol production carries the risk of food supply shock (Foust T. D., et al., 2009). The
second-generation fuel ethanol technology had been developed recently with agricultural wastes as raw materials that are largely produced every year in China, which can avoid the problem of grain competition. Whereas, the agricultural wastes with lignocellulose as the main component is hard to degrade during ethanol fermentation, because the structure of lignocellulose is complex and the effective biomass is difficult to release. So, it is necessary to apply complex pretreatment process on agricultural wastes for the second-generation fuel ethanol process. Therefore, it is significant to develop the high-efficient straw pretreatment technologies for the production of fuel ethanol from lignocellulose materials (Cao L. Y., et al., 2018). This paper reviewed the efficient pretreatment technologies of lignocellulose applied as the preparation process for fuel ethanol fermentation.

1.1 Lignocellulose pretreatment technologies
Lignocellulose mainly consists of cellulose, hemicellulose and lignin. In agricultural wastes, lignin and hemicellulose are covalently bonded and the cellulose molecules are encapsulated in them, and the complex structure increases the strength of the cell wall and protects the polysaccharides, making it difficult to be degraded (Zhang X. Y., et al., 2006). The hydrolysis efficiency can be improved by destroying the crystallinity of cellulose and degrading the reticular structure of lignin (Galbe M., et al., 2012; Viikari L., et al., 2012).

As the first step for ethanol production by lignocellulose, the pretreatment process with physical, chemical or biological methods could break the complex structure, which is benefit for cellulases and cellulose combination and also hydrolysis effect enhancement (Cao L. Y., et al., 2018). The reported pretreatment technologies in the literatures commonly include physical methods, dilute acid methods, dilute alkali methods, steam explosion methods, ammonia treatment methods, organic solvent methods, and ionic liquid method, etc, which are introduced as follows.

1.2 Physical method
Physical method is usually used to reduce the volume and increase the specific surface area of lignocellulose by mechanical force (Cao L. Y., et al., 2018). The microwave and ultrasonic were also applied in recent years as new physical pretreatment methods. Microwave method is easy to operate under the low energy requirement, and the heating could be achieved in a short time with small amount of inhibitor produced (Kumar A. K., et al., 2017). Ultrasonic pretreatment can change the physicochemical structure of wood and strengthen its enzymatic hydrolysis (He Z., et al., 2017).

1.3 Dilute acid pretreatment method
Dilute acid can catalyze the degradation of hemicellulose and destroy the structure of lignin and cellulose. A high efficiency could be achieved by dilute acid pretreatment, but large amount of waste water is produced accordingly and the corrosion of equipment is easily to occur, and also the production of inhibitor is high. These problems had reversely influenced the application of dilute acid pretreatment method. Based on dilute acid pretreatment technology, Zhang developed a new dry acid pretreatment method (Zhang J., et al., 2011). He found that when the ratio of dry matter to sulfuric acid solution was 2:1 (wt/wt) and the hot steam was directly injected at the temperature of 190 °C and pressure of 1.2 MPa for 3 min and the dry matter content of 50% (wt/wt), the solid content increased by an order of magnitude and the produced waste water was zero (He Y., et al., 2014). In order to eliminate the negative effects of the inhibitor, many studies was performed. A kerosene fungus strain *Amorphotheca resinae* ZN1 isolated by Zhang can quickly and effectively degrade all kinds of fermentation inhibitory toxins (Zhang J., et al., 2010). Amnuaycheewa et al replaced organic acids with dilute sulfuric acid in pretreatment, results showed that only a small number of inhibitors was produced and much more cellulose was efficiently hydrolyzed (Amnuaycheewa P., et al., 2017).

1.4 Dilute alkali pretreatment method
The dilute alkali could dissolve the acetyl and lignin in raw materials, and cellulose and hemicellulose can be released. The dilute alkali pretreatment process could be conducted in a relative mild condition,
but it would produce lots of wastewater. Li et al optimized the pretreatment conditions for combined dilute alkali and hydrogen peroxide pretreatment of Jerusalem artichoke straw, and results showed that the released cellulose content increased by 15% at 121 °C for 90 min with the combination of 4% hydrogen peroxide and 2% sodium hydroxide used (Li K., et al., 2016). Hosgun et al studied the effect of alkali pretreatment on hazelnut shell at low temperature (30 °C) and found that the percentage of 41.2% was removed and both sugar yield by enzymatic hydrolysis and ethanol yield increased accordingly (Hosgun E., et al., 2017). The alkali pretreatment of wheat straw was carried out at 80 °C by Tsegaye et al, and it was found that the dosage of sodium hydroxide was optimized, nearly 69.5% of lignin in the wheat straw could be removed by the alkali pretreatment and the further microorganism treatment (Tsegaye B., et al., 2017).

1.5 Steam pretreatment method
During the steam method, which is also called steam blasting pretreatment, the lignocellulose raw material is firstly heated by a high pressure steam, and then the pressure and steam is rapidly released, resulting in the rapidly expanded of materials and partial degradation of hemicellulose and lignin. The catalysts is unnecessary, but the cost of energy and equipment was required. Instant catapult steam explosion (ICSE) used super short time to reduce pressure, strengthen the mechanical force of explosion and reduce chemical by-reaction, so it could obtain a good pretreatment effect (Liu C.G., et al., 2014).

1.6 Ammonia pretreatment methods
Ammonia pretreatment methods includes ammonia water pretreatment method and ammonia fiber expansion pretreatment method. Ammonia Fiber Explosion (AFEX) is one of the most promising pretreatment methods for the consideration of industrial application (Eggeman T., et al., 2005). It has the similar principle with the steam explosion method but the pretreatment is realized by liquid ammonia gasification. In the process of ammonia explosion, the mechanical force is produced by rapid expansion in the gasification of liquid ammonia to ammonia gas. Besides, the alkalinity of ammonia helps destroy the chemical bond of lignocellulose. Ammonia-explosion pretreatment produced little inhibition, so the subsequent processes such as detoxification, washing and other steps are omitted. However, the recovery of ammonia gas need a lot of energy, ammonia gas corrodes the pretreatment equipment seriously under the condition of high temperature, so the equipment demand high quality.

Kamm has improved the AFEX process by replacing liquid ammonia with ammonia water (25%), and the enzymatic hydrolysis effect was improved (Kamm B., et al., 2017). Similar to dilute alkali, the ammonia water could dissolve the lignin and achieve the decomstruction of lignocellulosic raw material. This process requires relatively weak operating conditions, but produces a large amount of wastewater. Li et al used ultrasonic enhanced ammonia water to treat corncob, sorghum stalk and cornstalk at the ammonia concentration of 7.50-17.5 wt%, the sugar yield of corn cob was 40.5% in the optimum condition, and the reducing sugar yield for sorghum stalk and cornstalk was 47.1% and 44.1%, which increased by 25.7% and 30.8%, respectively (Li G. M., et al., 2016).

1.7 Organic solvent pretreatment method
The organic solvent such as methanol, ethylene glycol, acetone and others were used directly to treat lignocellulose or indirectly as catalyst by combination with acid or base during organic solvent pretreatment methods, which can remove lignin very well (F. Z., et al., 2018). Salapa et al compared the effects of the five organic solvents including ethanol, methanol, butanol, acetone and diethylene glycol on wheat straw pretreatment, and the results showed that ethanol pretreatment at 180 °C for 40min could obtain the largest amount of cellulose conversion (Salapa I., et al., 2017).

1.8 Ionic liquid pretreatment method
As a new solvent, ionic liquids can effectively dissolve and convert lignocellulose biomass. Ionic liquid pretreatment has become one of the most popular pretreatment methods in recent years (Chang
The rice straw was pretreated by 1-ethyl-3-methyl imidazolium acetate, and the glucose yield increased by 70% (Liu C. G., et al., 2016). Due to the high cost of ionic liquids, the large-scale industrial utilization is lack of economic feasibility. The mixture of ionic liquid and organic solvent was used in the study of Kahani et al, in order to reduce the usage of ionic liquid (Kahani S., et al., 2017). The recovery technology of ionic liquid can also significantly reduce the cost (Liang X., et al., 2017).

1.9 Biological pretreatment method
Enzymes produced by microbial physiological metabolism take a part in the destroying of the biomass structure, and the brown-rot fungi and white-rot fungi are the commonly microorganisms used in lignocellulose destruction (Vats S., et al., 2013). Kumar et al found that white-rot fungi can degrade lignin through the secreted peroxidase and laccase (Kumar R., et al., 2013). The biological pretreatment technology can be effectively promoted by the microbial flora selection and the genetic modification (Cao L. Y., et al., 2018).

2. Conclusion
The lignocellulose pretreatment is the necessary stage for ethanol production by agricultural waste, followed by the further hydrolysis process and fermentation process. The processes for lignocellulose pretreatment with the purpose of producing fuel ethanol by anaerobic fermentation were introduced in this paper. Although there has been great progress in the pretreatment and hydrolysis of lignocellulose at this stage, it still facing with the problems of high cost for practical application, low efficiency of transformation, and toxicant production so on, which need to be further developed.

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