

Pretreatment of Ligno-cellulosic Biomass for Biofuels and Bioproducts¹

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Introduction

Petroleum (or crude oil), a form of fossil fuel, is a nonrenewable energy. That means once petroleum is used, it cannot be regenerated at a pace to sustain its current consumption rate. Crude oil has taken 50–300 million years to form, but half of all global oil reserves have been consumed in approximately 125 years (Energy Insights 2011). The excessive use of petroleum results in severe environmental issues, such as greenhouse gas emissions, air pollution, and subsequent climate problems (Jun, Gillenwater, and Barbour 2001). Additionally, the United States depends on imported oil, which raises questions about energy security (Lefton and Weiss 2010). Considering all these factors, finding a clean and renewable liquid alternative fuel as a substitute for crude oil has become an urgent mission. Bioethanol is one option of these clean liquid fuels.

This EDIS publication discusses bioethanol as a renewable form of energy, explaining the importance of using ligno-cellulosic biomass to produce biofuels. It describes the pretreatment step in producing biofuels and the need for more research into this step so that ligno-cellulosic biofuels can be produced cheaply and efficiently at a commercial scale.

Why Bioethanol?

- Bioethanol is one form of renewable energy. It is renewable because it is made from bioresources like crops and agricultural residues, which can be grown in a short period of time.
- Ethanol has an octane number (99) that is higher than petroleum-based gasoline (80–100). A higher octane number indicates that the fuel can withstand more compression before engine knocking, which means ethanol generally has better engine performance (Gupta 2009). However, if ethanol absorbs water, the water can contaminate the fuel, resulting in engine damage and reduced fuel efficiency.
- Ethanol is burned more completely than other fuels, which results in less emission of greenhouse gases, such as nitrogen oxides and carbon dioxide (Gupta 2009). On the other hand, the energy content of ethanol is approximately 33% lower than gasoline, which results in vehicles getting less mileage from ethanol.
- Adopting bioethanol is relatively easy because it can be integrated into the existing road transport fuel system. In the United States, ethanol can be blended with gasoline at rates of up to 10%.

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Why Ligno-Cellulosic Bioethanol?

- Lignocellulose is the nonedible part of plants. Using lignocellulose to produce ethanol avoids competition with the food industry, as opposed to first generation biofuels, which are directly converted from sugar and starch crops found in arable areas (Hamelinck, Geertje, and Faaij 2005).
- Lignocellulose is the most abundant renewable biomass. The yield of lignocellulose can reach approximately 200 billion metric tons worldwide per year (Zhang et al. 2007).
- Lignocellulose is a feedstock with a low production cost. Lignocellulose can be found everywhere and is available as waste biomass, including agricultural residues (wheat straw, sugarcane bagasse, and corn stover), energy crops (switch grass), and municipal solid waste (paper and paperboard products) (Hamelinck, Geertje, and Faaij 2005).
- Cellulosic ethanol has a larger net energy gain than corn ethanol. The net energy of biofuel is defined as the difference between the consumable energy of biofuel produced and the energy expended during biofuel production (Farrell et al. 2006).

The process of producing cellulosic ethanol is generally divided into four steps: 1) pretreatment, 2) enzyme hydrolysis, 3) fermentation, and 4) distillation. For more information on the steps to produce cellulosic ethanol, see the EDIS publication AE493 – *How Ethanol Is Made from Cellulosic Biomass* (<http://edis.ifas.ufl.edu/ae493>).

Although pretreatment is the first step, it is one of the most expensive parts of the entire bioethanol process. The following sections describe the need for the pretreatment process, discuss the different types of pretreatment methods, and show the need for a cost-effective and efficient pretreatment method that can scale up to commercial production.

Why Do We Need Pretreatment?

Pretreatment is a combination of many processes. It consists of a size reduction step followed by chemical, biological, or physical treatments. As shown in Figure 1, lignocellulose is mainly made up of lignin, hemicellulose, and cellulose fibers. These all combine to form a firm, compact network structure. In a natural state, after size reduction, the access to cellulose is still blocked by lignin and hemicellulose because of the intact cell wall structure. Moreover, cellulose has a highly crystalline structure that is difficult to break down (Hsu, Ladisch, and Tsao 1980).

The purpose of pretreatment is to destroy the structure of cellulosic biomass plant cell walls and make cellulose more accessible to the subsequent process of hydrolysis (during hydrolysis, cellulose is broken down into simple sugars).

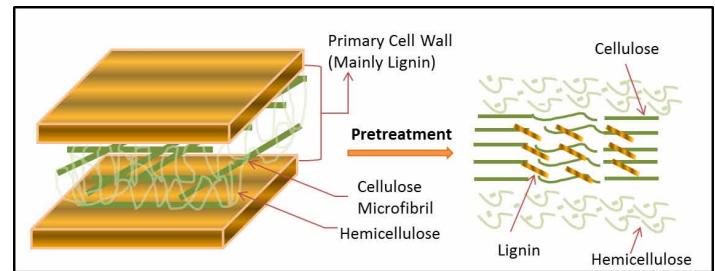


Figure 1. Schematic diagram showing the effect of pretreatment on ligno-cellulosic biomass. The primary cell wall becomes compacted by a dense lignin network structure as the plant grows and ages.

Credits: Zhaohui Tong

What Are the Key Factors for Pretreatment?

Because pretreatment is the first step of the bioethanol process for ligno-cellulosic biomass, the quality and efficiency of pretreatment directly affect the subsequent steps, including enzyme hydrolysis and fermentation steps. A high-efficiency pretreatment is determined by the following key factors (Kumar et al. 2009):

1. **High yield for a particular feedstock.** Each feedstock has a different resistance to acid, base, and heat. For example, breaking down wood is more difficult than breaking down agricultural residues. Using the right pretreatment method for a particular feedstock is essential.
2. **High sugar concentration.** High sugar concentration usually indicates a high ethanol yield since only simple sugars can be converted into ethanol by fermentation. An efficient pretreatment can obtain a high single sugar yield by avoiding the degradation or loss of polymer sugars.
3. **The increase of enzyme and fermentation compatibility.** The pretreatment process usually increases the surface area and the pore size of cell walls, resulting in easier contact between the enzyme and cellulose. It is also important to generate fewer chemicals that are toxic to the subsequent fermentation process.
4. **Minimum cost.** Possible methods to minimize the cost of pretreatment include using inexpensive and less corrosive chemicals, decreasing energy consumption by applying less power and heat, and avoiding energy-intensive size-reduction processes.

5. **Ability to scale to commercial production.** The ultimate goal for the cellulosic bioethanol process is that it can be scaled up for commercial production. Pretreatment units cost the most in a bioethanol production facility. Therefore, it is essential to develop a pretreatment process that is easy and cost-effective to scale to commercial production.

Pretreatment Methods

Pretreatment methods can be categorized into four types: physical methods (e.g., milling and grinding); physico-chemical methods (e.g., steam explosion or hydrothermolysis); chemical methods (e.g., using acids, alkali, oxidizing agents, or organic solvents to treat biomass); and biological methods (e.g., using microorganisms and fungi to treat biomass) (Kumar et al. 2009). Several typical pretreatment methods are described in the following sections.

Steam Explosion Pretreatment

Steam explosion pretreatment is the most commonly used method for lignocelluloses, especially in processes scaled for commercial production. After a size reduction, biomass is rapidly heated by a high-pressure saturated steam with or without chemicals. After the biomass is held at this pressure for a few minutes, the pressure is suddenly released and materials undergo an explosive decompression. The “explosion” improves the accessibility of feedstocks by removing hemicelluloses and increasing surface areas to allow enzyme penetration (Sun and Cheng 2002).

Steam explosion pretreatment has advantages and limitations. Steam rapidly heats the biomass to the target temperature without excessive dilution of the resulting sugars (Mosier et al. 2005). This method uses less hazardous chemicals and conditions, reducing the environmental impact (Avellar and Glasser 1998). However, the steam explosion method does have its drawbacks, such as incomplete disruption of lignin and the generation of toxic chemicals, which may affect the downstream processes.

Dilute Acid Pretreatment

Dilute acid pretreatment has been used for many years and has recently been intensively investigated. In this method, acid is used in a low concentration at a high temperature to dissolve hemicelluloses from biomass cell walls, rendering celluloses more accessible to enzymes (Alvira et al. 2010). The processing conditions can be adjusted according to the feedstock type, reaction temperature, reaction time, etc. The acids used to pretreat lignocelluloses include sulfuric acid, nitric acid, hydrochloric acid, and phosphoric acid.

Pretreatment using dilute acid is favorable for scale-up production of biofuels because of its high efficiency to convert most of the hemicellulose into soluble sugars and the use of cheap chemicals (Kumar et al. 2009). However, the process generates degraded chemicals (e.g., furfural and phenolic components) that are toxic to the downstream processes. In addition, the generation of low-quality lignin and the need for an extra neutralization step before fermentation impeded the development of acid treatment (Mosier et al. 2005).

Organosolv Pretreatment

Organosolv pretreatment is a pulping technique that dissolves lignin and hemicellulose in an organic solvent while cellulose remains as undissolved solids. The most commonly used organic solvents are methanol and ethanol because of their low cost, low boiling point, and miscibility with water. The benefits of organosolv pretreatment include the ability to be used with all types of feedstocks, the production of high-quality lignin by-products, the ability to easily recycle the solvent (e.g., ethanol), and the minimum loss of celluloses and chemicals from hemicelluloses. However, organosolv pretreatment is limited because of the high operation cost and high cost of organic solvent (Zhao, Cheng, and Liu 2009).

Ammonia Fiber Explosion (AFEX) Pretreatment

The AFEX pretreatment method is quite similar to the steam explosion method. In AFEX pretreatment, lignocellulosic biomass is exposed to liquid ammonia at a moderate temperature (60°C–100°C) and a high pressure (250–300 psi) for a period of time, and then the pressure is suddenly reduced. This method generates high surface areas and results in better digestibility and enzyme accessibility (e.g., cellulase) (Teymouri et al. 2005). Also, no toxic chemicals are generated for downstream processes. However, it does not significantly remove hemicelluloses, which may reduce enzyme accessibility and final sugar yield (Zhang et al. 2007).

Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose (SPORL)

In this pretreatment method, wood chips and the pretreatment solution, along with sulfite-based chemicals, are mixed together at a high temperature. This is followed by a size-reduction process to generate fibrous substrates for subsequent saccharification and fermentation (Zhu et al. 2009). The SPORL method has a number of advantages: 1) robust method for pretreating woody biomass (i.e., materials that are hard to break down); 2) reduced reactor

corrosion problems; and 3) ability to easily scale to commercial production (Wang et al. 2009). Although this method has these advantages, there are also clear limitations, including the high dosage of chemicals and the high cost of chemical recovery systems. Moreover, the chemicals produced in this process are toxic to downstream processes.

Conclusion

The pretreatment step plays a significant role in a lignocellulosic biorefinery process. Currently many efforts are devoted to developing new technologies to further decrease the cost of pretreatment and generate less toxic chemicals, higher sugar yield, and higher-value by-products. The choice of the pretreatment technology depends on a variety of factors, such as the type of biomass, the value of by-products, and the process complexity. The combination of different methods may yield more positive effects in the future.

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