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How Ethanol Is Made from Cellulosic Biomass[1]

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Introduction

Energy demand is predicted to grow more than 50% by 2025 because of the emerging demand from several rapidly developing nations (Ragauskas et al. 2006). Our main energy resource, petroleum oil, is being depleted quickly in the United States and around the world. The day is not far when we will be very close to "peak oil," the point at which oil demand will exceed oil supply. Surplus oil production is nearly disappearing, and as early as 2015, the shortfall in output could reach nearly 10 million barrels per day (Energy Bulletin 2010). Eventually, petroleum reserves will be completely depleted. This future scenario acts as a strong motivation to look for alternative and renewable resources to meet the ever-growing demand for energy.

Fuel ethanol is a liquid fuel that contains more than 99% ethanol. Toxic additives are added to fuel ethanol so that it cannot be used as a source of beverage alcohol. It can also be used as an additive substitute in other liquid fuels. For example, in the United States, E10 gasoline is gasoline blended with a concentration of 10% ethanol, and E85 gasoline is gasoline with 85% ethanol.

Ethanol can be derived from sugar-based, corn-based, and cellulose-based materials (feedstocks). Production of ethanol from sugar and corn feedstocks is often viewed as competing with food production and increasing prices of food and fuel. Therefore, ethanol from cellulose-based biomass has been attracting interest because using non-edible biomass as a feedstock to produce ethanol minimizes competition with the food industry. In fact, a U.S. Department of Agriculture and U.S. Department of Energy study concluded that at least 1 billion tons of cellulose in the form of straw, corn stover, other forage residues, and wood wastes could be sustainably collected and processed in the United States each year. This would produce 67 billion gallons of ethanol annually, replacing 30% of gasoline consumption in the United States (U.S. Department of Energy, EERE 2012). Florida has large amounts of cellulosic biomass resources that could be converted to fuel (e.g., ethanol).

UF/IFAS built a cellulosic bioethanol pilot plant on the University of Florida campus to study how Florida could use these cellulosic biomass resources. In 2012, UF/IFAS partnered with Buckeye Technologies, Inc., to build the Stan Mayfield Biorefinery Pilot Plant in Perry, Florida, which has scaled-up the process of the campus pilot plant. This EDIS publication provides a general overview of the production process for manufacturing ethanol from cellulosic biomass, including its constituents, conversion processes, and final products.

Cellulosic Biomass

Cellulosic biomass is the structural portion of plants, including complex sugars that cannot directly be used for food ingredients or fermentation substrates. According to the U.S. Department of Energy (EERE Biomass Program

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2012), cellulosic biomass can be obtained from a variety of sources, such as:

- Agricultural residues (corn stover, sugarcane bagasse, spent sugar beet pulp and sweet sorghum, etc.)
- Forestry residues (fallen branches, leaves, twigs, saw dust, etc.)
- Municipal solid waste (paper and paperboard products)
- Industrial wastes (papermaking sludge)
- Agricultural feedstocks grown as energy crops (herbaceous and woody crops, such as switchgrass, fast-growing hybrid poplar and leucaena trees, etc.)

Three main components — cellulose, hemicellulose, and lignin — make up the cell walls that form the tissue structure of cellulosic biomass. These cell walls also include a small amount of pectin, waxes, water soluble sugars, and organic acids (Rowell 2005). The three main components (cellulose, hemicellulose, and lignin) are interwoven to form the networking structure of the plant cell wall. Converting cellulosic biomass to biofuels such as ethanol essentially involves breaking down the plant cell wall network structure and releasing the simple sugars that are subsequently fermented by bacteria or yeast to ethanol (Geddes et al. 2010).

Constituents of Cellulosic Biomass

Cellulose

As the most common organic compound on Earth, cellulose comprises 38%–50% of cellulosic biomass (Rowell 2005). Cellulose is a polymer of 6-carbon sugar molecules (glucose) linked together in a crystal structure that strengthens plants and is similar in function to skeletons of animals. Cellulose is the major constituent of paper, paperboard, card stock, and textiles, all of which are made from woody or herbaceous biomass such as pine, eucalyptus, sugarcane bagasse, cotton, or linen. In a bioethanol process, cellulose must first be transformed into easily-fermentable monosaccharides (simple sugars, such as glucoses) by physical, chemical, and biological treatments, and then used as a fermentation substrate to produce ethanol through a fermentation process.

Hemicellulose

Hemicellulose forms 23%–32% of cellulosic biomass (Rowell 2005), and is present, along with cellulose, in almost all plant cell walls. It consists of complex polysaccharides from a variety of five- and six-carbon sugars. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength.

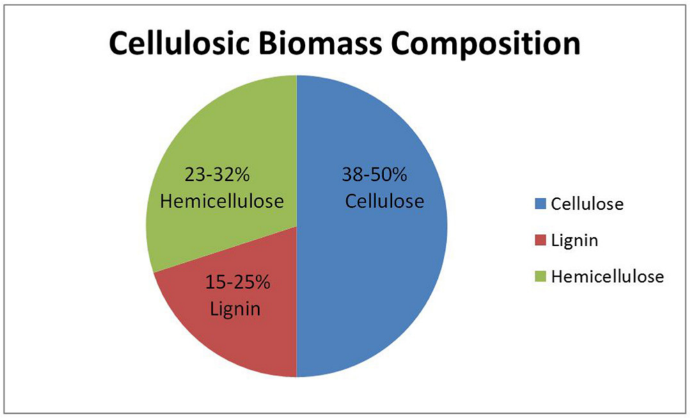

Figure 1. Composition of Cellulosic Biomass

Hemicellulose is easily hydrolyzed by dilute acid or base, as well as a myriad of hemicellulase enzymes. However, five-carbon sugars released from hemicelluloses have more difficulty fermenting than 6-carbon sugars.

Lignin

Lignin forms 15%–25% of cellulosic biomass. It is a complex network polymer with phenyl propane basic units. Lignin has a variety of chemical structures, depending on different purification approaches. It fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. It is covalently linked to hemicellulose and thereby cross-linked with different plant polysaccharides. As a rigid material, lignin provides mechanical strength to the cell wall, and also plays a crucial part in conducting water through the plant stems (Rowell 2005). During a bioethanol process, lignin is left as a residue. However, it still has some energy value and can be used to make a variety of value-added products.

Bioethanol

Bioethanol (fuel ethanol from renewable biomass) has many advantages over fossil fuels:

- It is renewable and environmentally-friendly, which allows less greenhouse gas emissions and no net CO_2 emissions.
- It has better engine performance because of its higher octane number. The octane number is a measure of the resistance to auto-ignition in fuels used in spark-ignition internal combustion engines. Higher octane number means the engine delivers greater horsepower in a given stroke of the cylinder (displacement).

Cellulosic Bioethanol Process

The cellulosic bioethanol process consists of four steps: 1) pretreatment, 2) enzyme hydrolysis, 3) fermentation, and 4) distillation. See Figure 2 for an illustration of the process.

Pretreatment

Pretreatment is the first step of the cellulosic bioethanol process. The purpose of pretreatment is to make the cellulose more susceptible to being broken down so that it is ready for the enzyme hydrolysis step. Pretreatment does this by partially removing the lignin and hemicellulose, which block the cellulose inside the cell wall (Geddes et al. 2010). Currently, there are a number of challenges to efficiently and effectively completing the pretreatment process, including the following (Chandra et al. 2007; Mosier et al. 2005):

- Reducing the cost (capital and operating) of the process;
- Ensuring that the particle size is reduced enough in order to increase surface area-to-mass ratio for maximum exposure to contact surfaces;
- Minimizing the accumulation of inhibitory products that could interfere with the subsequent fermentation step;
- Enhancing the sugar yield and allowing efficient hydrolysis at a lower concentration of enzyme.

The pretreatment step can be done by using acid, alkali, organic solvents, heat treatments, etc. Some options for pretreatment are steam explosion, liquid hot water, lime-ammonia and acid treatment (Wyman 2010).

Enzyme Hydrolysis

Enzyme hydrolysis usually occurs immediately after the pretreatment step. Enzyme hydrolysis is the process used to convert polysaccharides (cellulose and hemicelluloses) and their oligomers (molecules with a few single sugar units) into simple sugars, which can be fermented by bacteria or yeast. The high cost of enzymes is currently the greatest challenge in this processing step. Although current world-leading enzyme suppliers have reduced the price of enzymes about 20- to 30-fold, the cost for enzymes is still the most expensive part of the entire bioethanol process. An important approach to reduce the cost for enzyme hydrolysis is to develop an efficient pretreatment method to reduce the enzyme dosage and enhance the yield of simple sugars. Sugar yield is typically less than 20% without pretreatment, whereas yield after pretreatment often exceeds 90% (Chandra et al. 2007).

Fermentation

Conventional fermentation is the process that converts the sugars from sugar-rich feedstocks (fruit juices, pomace and grains, such as corn and sweet sorghum) into alcohol in the brewing and beverage alcohol industries. In a cellulosic bioethanol process, fermentation is used to convert the single sugars obtained from the enzyme hydrolysis step (glucose from cellulose and xylose from hemicellulose) to fuel ethanol. Organisms such as yeast (*Saccharomyces cerevisiae*) or bacteria (*Escherichia coli*) are used to convert these simple sugars to ethanol. In order to keep distillation costs low, the appropriate microorganism is selected based on the need to achieve high ethanol yield while also withstanding inhibition from accumulating toxic substances and autointoxication from increasing ethanol concentration.

The fermentation step usually follows enzymatic hydrolysis, as a separate step. This procedure is known as separate hydrolysis and fermentation (SHF). However, the most commonly used technique is called the simultaneous saccharification and fermentation (SSF) process, which is carried out by combining fermentation and enzyme hydrolysis in the same step. Normally, higher ethanol yield can be achieved with SSF, which can be attributed to the reduction

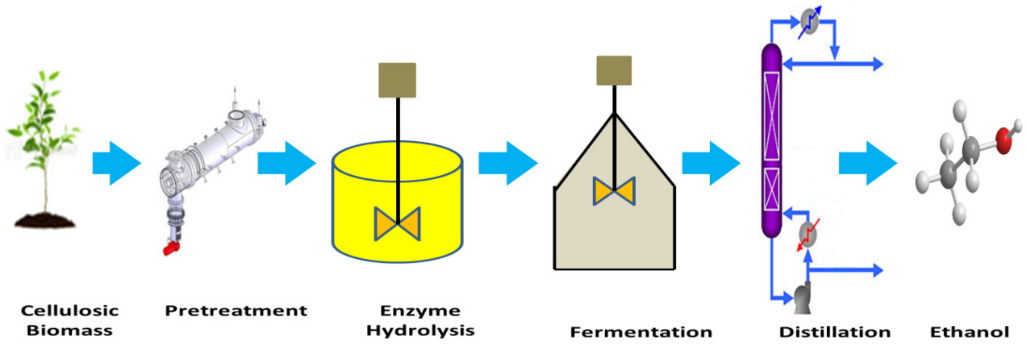

Figure 2. Schematic of Cellulosic Ethanol Processes

of inhibitory end-products (glucose and cellubiose) (Olofsson, Bertilsson, and Lidén 2008).

Distillation

Ethanol is recovered from the fermentation broth by the process called distillation. Distillation works by boiling the liquid mixture of water and ethanol. Ethanol vapors are separated from the liquid portion because ethanol has a lower boiling point (78.3°C) at atmospheric pressure compared to water (100°C). The lignin residues, along with unreacted cellulose, hemicellulose, ash, enzymes, and remaining microorganisms, end up in the bottom of the distillation column during the bioethanol process. This solid waste (still bottoms) has high energy content, which can be burned as fuel for power or may be converted to various value-added products.

Fuel Ethanol

Ethanol is used as alcohol in common usage and now is also used as transportation fuel. The largest single use of ethanol as a fuel is as a motor fuel and fuel additive. The United States uses E10 gasoline/ethanol mixtures for conventional gasoline engine vehicles and E85 for flexible fuel vehicles. The blending of ethanol makes the fuel mixture burn more completely and reduces pollution emissions. However, the energy content of ethanol is approximately 33% lower than gasoline. If you use E10 gasoline/ethanol mixture instead of pure gasoline, the mileage may decrease 3.3% (EIA 2012). Blending must be done very carefully, and it is usually done locally. Ethanol easily absorbs water if underground pipes have any leaks. It can also absorb water vapor if there are any loose seals. Water does not mix with oil and phase separation will occur. Water contamination may result in engine damage and reduction of fuel efficiency.

Conclusion

Producing fuel ethanol from inedible and abundantly-available cellulose biomass offers an important opportunity to sustainably produce alternative transportation fuels. This would be extremely beneficial from economic and environmental standpoints. Although significant progress has been made to reduce the manufacturing costs, widespread commercialization of this technology has not been realized. Before bioethanol can become an economic alternative for transportation fuel, there will need to be more efficient pretreatment methods, further reduction of biological enzyme costs, and development of more efficient genetically engineered microorganisms. Also, the biofuels industry needs ways to combine integrated production technologies and produce value-added byproducts. If these goals are met, then bioethanol could become a viable economic choice as a transportation fuel that also reduces greenhouse gas emissions.

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