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# Ethanol From Cellulose: A General Review

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## INTRODUCTION

The use of ethanol as an alternative motor fuel has been steadily increasing around the world for a number of reasons. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide buildup. Ethanol, unlike gasoline, is an oxygenated fuel that contains 35% oxygen, which reduces particulate and NOx emissions from combustion.

Ethanol can be made synthetically from petroleum or by microbial conversion of biomass materials through fermentation. In 1995, about 93% of the ethanol in the world was produced by the fermentation method and about 7% by the synthetic method. The fermentation method generally uses three steps: (1) the formation of a solution of fermentable sugars, (2) the fermentation of these sugars to ethanol, and (3) the separation and purification of the ethanol, usually by distillation.

## SUGAR FEEDSTOCKS

Fermentation involves microorganisms that use the fermentable sugars for food and in the process produces ethanol and other byproducts. These microorganisms can typically use the 6-carbon sugars, one of the most common being glucose. Therefore, biomass materials containing high levels of glucose or precursors to glucose are the easiest to convert to ethanol. However, since sugar materials are in the human food chain, these materials are usually too expensive to use for ethanol production.

One example of a sugar feedstock is sugarcane. Brazil developed a successful fuel ethanol program from sugarcane for a number of reasons: (1) Brazil traditionally relied heavily on imported oil for transportation fuels, which caused a severe economic drain on the country; (2) Brazil can attain very high yields of sugarcane; and (3) Brazil has also experienced periods of poor sugar markets. As a result, the Brazilian government established programs supportive of the industry with the result that Brazil has been able to successfully produce and use sugarcane for fuel ethanol production.

Although fungi, bacteria, and yeast microorganisms can be used for fermentation, a specific yeast (*Saccharomyces cerevisiae* also known as Bakers' yeast, since it is commonly used in the baking industry) is frequently used to ferment glucose to ethanol. Theoretically, 100 grams of glucose will produce 51.4 g of ethanol and 48.8 g of carbon dioxide. However, in practice, the microorganisms use some of the glucose for growth and the actual yield is less than 100%.

Other biomass feedstocks rich in sugars (materials known as saccharides) include sugar beet, sweet sorghum, and various fruits. However, these materials are all in the human food chain and, except for some processing residues are generally too expensive to use for fuel ethanol production.

## STARCHY FEEDSTOCKS

Another potential ethanol feedstock is starch. Starch molecules are made up of long chains of glucose molecules. Thus, starchy materials can also be fermented after breaking starch molecules into simple glucose molecules. Examples of starchy materials commonly used around the world for ethanol production include cereal grains, potato, sweet potato, and cassava. Cereal grains commonly used in the US for ethanol production include maize and wheat.

Approximately 475 million tonnes of maize were produced in the world in 1990 with about 200 million t produced in the US. Approximately 8 to 9 million t, or 4% of US maize grain went into ethanol in 1990. A bushel of maize grain (25.3 kg or 56 lb. at 15% moisture) can produce from 9.4 to 10.9 L (2.5 to 2.9 gallons) of pure ethanol, depending on the technology used.

Starchy materials require a reaction of starch with water (hydrolysis) to break down the starch into fermentable sugars (saccharification). Typically, hydrolysis is performed by mixing the starch with water to

form a slurry which is then stirred and heated to rupture the cell walls. Specific enzymes that will break the chemical bonds are added at various times during the heating cycle.

## CELLULOSIC FEEDSTOCKS

Like sugar materials, starchy materials are also in the human food chain and are thus expensive. Fortunately, a third alternative exists—cellulosic materials. Examples of cellulosic materials are paper, cardboard, wood, and other fibrous plant material.

Cellulosic resources are in general very widespread and abundant. For example, forests comprise about 80% of the world's biomass. Being abundant and outside the human food chain makes cellulosic materials relatively inexpensive feedstocks for ethanol production.

Cellulosic materials are comprised of lignin, hemicellulose, and cellulose and are thus sometimes called lignocellulosic materials. One of the primary functions of lignin is to provide structural support for the plant. Thus, in general, trees have higher lignin contents then grasses. Unfortunately, lignin which contains no sugars, encloses the cellulose and hemicellulose molecules, making them difficult to reach.

Cellulose molecules consist of long chains of glucose molecules as do starch molecules, but have a different structural configuration. These structural characteristics plus the encapsulation by lignin makes cellulosic materials more difficult to hydrolyze than starchy materials.

Hemicellulose is also comprised of long chains of sugar molecules; but contains, in addition to glucose (a 6-carbon or hexose sugar), contains pentoses (5-carbon sugars). To complicate matters, the exact sugar composition of hemicellulose can vary depending on the type of plant.

Since 5-carbon sugars comprise a high percentage of the available sugars, the ability to recover and ferment them into ethanol is important for the efficiency and economics of the process. Recently, special microorganisms have been genetically engineered which can ferment 5-carbon sugars into ethanol with relatively high efficiency.

One example is a genetically engineered microorganism developed by the University of Florida that has the ability to ferment both 5- and 6-carbon sugars. This microorganism was issued US patent 5,000,000. Other researchers have developed microorganisms with the ability to efficiently ferment at least part of the sugars present.

Bacteria have drawn special attention from researchers because of their speed of fermentation. In general, bacteria can ferment in minutes as compared to hours for yeast.

## ETHANOL-FROM-CELLULOSE

In times of fuel shortages, fermentation ethanol has been commercially manufactured in the US from cellulosic biomass feedstocks using acid hydrolysis techniques. Currently, some countries in locations with higher ethanol and fuel prices, are producing ethanol from cellulosic feedstocks. However, it is only recently that cost-effective technologies for producing ethanol-from-cellulose (EFC) in the US have started to emerge.

There are three basic types of EFC processes—acid hydrolysis, enzymatic hydrolysis, and thermochemical—with variations for each. The most common is acid hydrolysis. Virtually any acid can be used; however, sulfuric acid is most commonly used since it is usually the least expensive.

## ACID HYDROLYSIS

There are two basic types of acid processes: dilute acid and concentrated acid, each with variations. Dilute acid processes are conducted under high temperature and pressure, and have reaction times in the range of seconds or minutes, which facilitates continuous processing.

As an example, using a dilute acid process with 1% sulfuric acid in a continuous flow reactor at a residence time of 0.22 minutes and a temperature of 237°C (458°F) with pure cellulose provided a yield over 50% sugars. In this case, 0.9 t (1 ton) of dry wood would yield about 189 L (50 gallons) of pure ethanol. The combination of acid and high temperature and pressure dictate special reactor materials, which can make the reactor expensive.

Most dilute acid processes are limited to a sugar recovery efficiency of around 50%. The reason for this is that at least two reactions are part of this process. The first reaction converts the cellulosic materials to

sugar and the second reaction converts the sugars to other chemicals. Unfortunately, the conditions that cause the first reaction to occur also are the right conditions for the second to occur. Thus, once the cellulosic molecules are broken apart, the reaction proceeds rapidly to break down the sugars into other products—most notably furfural, a chemical used in the plastics industry. Not only does sugar degradation reduce sugar yield, but the furfural and other degradation products can be poisonous to the fermentation microorganisms.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Their biggest disadvantage is their low sugar yield. For rapid continuous processes, in order to allow adequate acid penetration, feedstocks must also be reduced in size so that the maximum particle dimension is in the range of a few millimeters.

Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars. Unfortunately, sugar degradation is still a problem and yields are limited to around 272 L/t (80 gallons of ethanol/ton) of dry wood.

The concentrated acid process uses relatively mild temperatures and the only pressures involved are usually only those created by pumping materials from vessel to vessel. One concentrated acid process was first developed by USDA and further refined by Purdue University and the Tennessee Valley Authority.

In the TVA concentrated acid process, corn stover is mixed with dilute (10%) sulfuric acid, and heated to 100ºC for 2 to 6 hours in the first (or hemicellulose) hydrolysis reactor. The low temperatures and pressures minimize the degradation of sugars. To recover the sugars, the hydrolyzed material in the first reactor is soaked in water and drained several times.

The solid residue from the first stage is then dewatered and soaked in a 30% to 40% concentration of sulfuric acid for 1 to 4 hr as a pre-cellulose hydrolysis step. This material is then dewatered and dried with the effect that the acid concentration in the material is increased to about 70%. After reacting in another vessel for 1 to 4 hr at 100ºC, the reactor contents are filtered to remove solids and recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage hydrolysis. The sugars from the second stage hydrolysis are thus recovered in the liquid from the first stage hydrolysis.

The primary advantage of the concentrated process is the high sugar recovery efficiency, which can be on the order of over 90% of both hemicellulose and cellulose sugars. The low temperatures and pressures employed also allow the use of relatively low cost materials such as fiberglass tanks and piping. Unfortunately, it is a relatively slow process and cost effective acid recovery systems have been difficult to develop. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization forms large quantities of calcium sulfate, which requires disposal and creates additional expense.

Using some assumed cellulose conversion and fermentation efficiencies, ethanol yields from glucose can be calculated for corn stover (the above-ground part of the corn plant less the ears) as shown in Table 1 showing ethanol yield from glucose. Similarly, ethanol yields from the xylose can be calculated as shown in Table 2.

Thus, in this example, the total yield/t of dry stover is about 227 L (60 gallons) of ethanol. These numbers also show how critical sugar conversion and recovery efficiencies and fermentation efficiencies are. If one could attain 95% for both efficiencies, then the yield would be approximately 350 L/t (103 gallons of ethanol/ton).

**Table 1.** Ethanol yield from glucose.

| | |
|---|---|
| Dry stover | 1 tonne (1000 kg) |
| Cellulose content | × 0.45 |
| Cellulose conversion and recovery efficiency | × 0.76 |
| Ethanol stoichiometric yield | × 0.51 |
| Glucose fermentation efficiency | × 0.75 |
| Yield from glucose | 131 kg ethanol = 151 L (40 gallons) |

**Table 2.** Ethanol yield from xylose.

| | |
|---|---|
| Dry stover | 1 tonne (1000 kg) |
| Hemicellulose content | × 0.29 |
| Hemicellulose conversion and recovery efficiency | × 0.90 |
| Ethanol stoichiometric yield | × 0.51 |
| Xylose fermentation efficiency | × 0.50 |
| Yield from xylose | 66 kg ethanol = 76 L (20 gallons) |

## ENZYMATIC HYDROLYSIS

Another basic method of hydrolysis is enzymatic hydrolysis. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. However, for enzymes to work, they must obtain access to the molecules to be hydrolyzed. For enzymatic processes to be effective, some kind of pretreatment process is thus needed to break the crystalline structure of the lignocellulose and remove the lignin to expose the cellulose and hemicellulose molecules. Depending on the biomass material, either physical or chemical pretreatment methods may be used.

Physical methods may use high temperature and pressure, milling, radiation, or freezing—all of which require high-energy consumption. The chemical method uses a solvent to break apart and dissolve the crystalline structure.

An example of an enzymatic hydrolysis-based process is under development by the National Renewable Energy Laboratory (NREL). After a dilute acid pretreatment, the slurry is detoxified to remove materials that would be poisonous to the microorganisms used in the process. A small part of this slurry is sent to a separate vessel that is used to grow microorganisms that produce the cellulase enzyme for the process. Another part of the slurry is sent to another vessel to maintain and grow a yeast culture for fermentation. In the NREL process, both enzymes and the fermentation microorganisms are added at the same time to the slurry, and sugar conversion and fermentation occur simultaneously in a process called simultaneous saccharification and cofermentation (SSCF).

Due to the tough crystalline structure, the enzymes currently available require several days to achieve good results. Since long process times tie up reactor vessels for long periods, these vessels have to either be quite large or many of them must be used. Either option is expensive. Currently the cost of enzymes is also too high and research is continuing to bring down the cost of enzymes.

However, if less expensive enzymes can be developed enzymatic processes hold several advantages: (1) their efficiency is quite high and their byproduct production can be controlled; (2) their mild process conditions do not require expensive materials of construction; and (3) their process energy requirements are relatively low.

## THERMOCHEMICAL PROCESSES

There are two ethanol production processes that currently employ thermochemical reactions in their processes. The first system is actually a hybrid thermochemical and biological system. An example is a process under development by Bioengineering Resources in Fayetteville, Arkansas. Biomass materials are first thermochemically gasified and the synthesis gas (a mixture of hydrogen and carbon oxides) bubbled through specially designed fermenters. A microorganism that is capable of converting the synthesis gas is introduced into the fermenters under specific process conditions to cause fermentation to ethanol.

The second thermochemical ethanol production process does not use any microorganisms. In this process, biomass materials are first thermochemically gasified and the synthesis gas passed through a reactor containing catalysts, which cause the gas to be converted into ethanol. An intensive effort was made by Germany in World War II to develop these processes for fuel. Numerous efforts have been made since then to develop commercially viable thermochemical-to-ethanol processes.

Ethanol yields up to 50% have been obtained using synthesis gas-to-ethanol processes. Some processes that first produce methanol and then use catalytic shifts to produce ethanol have obtained ethanol yields in the

**Table 3.** A partial listing of companies developing ethanol-from-cellulose technologies.

| Company & headquarters location | Technology | Primary feedstock | Ethanol capacity | Comments |
|---|---|---|---|---|
| BCI, Dedham, MA | Dilute acid | Bagasse | 7560 million L/yr (20 million gpy[z]) | Plant to break ground in 2002 |
| Bioengineering Resources, Fayetteville, AR | Thermochemical gasification with fermentation | | | Pilot plant operating |
| Ethxx International, Aurora, ON | Thermochemical gasification with catalytic conversion | Wood | | Pilot plant operating |
| Fuel Cell Energy, Lakewood, CO | Thermochemical gasification with catalytic conversion | Wood | | Pilot plant operating |
| Iogen, Ottawa, ON | Enzymatic | Oat hulls, switchgrass, wheat straw, and corn stover | 378 million L/yr (1 million gpy) | Experimental plant operating |
| Masada, Birmingham, AL | Concentrated acid | MSW | 3780 million L/yr (10 million gpy) | Plant to break ground early 2002 |
| Paszner Technologies, Inc, Surrey, BC | Acidified aqueous acetone process | Wood | | Commercial plants under construction |
| PureVision Technology, Ft. Lupton, CO | Enzymatic | Wood | | Constructing pilot plant |

[z]gpy=gallons per year

range of 80%. Unfortunately, like the other processes, finding a cost-effective all-thermochemical process has been difficult.

## COMMERCIALIZATION EFFORTS

Several EFC plants were built and operated in various countries in World War II, when wartime conditions changed economic conditions and priorities. These countries included Germany, Russia, China, Korea, Switzerland, the United States, and other countries. Today, due to competition from synthetically produced ethanol, only a few of these plants are still operating with virtually all of them in Russia.

A paper manufacturing plant in Temi-schammaig, Quebec, operates off of byproduct sugars contained in "sulfite liquor," which contains about 2% fermentable sugars. This is the only facility of its kind in North America. This facility is operated by Tembec, Inc., and produces 4 million gallons per year of industrial grade ethanol.

Several efforts are underway in North America to commercially produce ethanol from wood and other cellulosic materials as a primary product. Table 3 partially summarizes these companies and their activities, which are in various states of progress.

## SUMMARY

Ethanol-from-cellulose (EFC) holds great potential due to the widespread availability, abundance, and relatively low cost of cellulosic materials. However, although several EFC processes are technically feasible, cost-effective processes have been difficult to achieve. Only recently have cost-effective EFC technologies begun to emerge.