Conversion of Corn-Kernel Fiber in Conventional Fuel-Ethanol Plants

National Corn to Ethanol Research Center

Executive Summary

Ethanol derived from corn-kernel fiber is qualified as cellulosic biofuel since its production results in a 60% reduction in greenhouse gas production relative to a 2005 baseline for petroleum fuels according to the Renewable Fuel Standard (RFS) (U.S. EPA). A conventional fuel-ethanol plant can achieve a potential 9% increase in ethanol production (compared with the starch based ethanol), if they can successfully convert and ferment the cellulose and hemicellulose (xylose and galactose) in corn-kernel fiber; and achieve an additional 3% increase in ethanol production if they can ferment the arabinose derived from hemicellulose. Although complete conversion of all the corn-kernel fiber sugars to ethanol (total of 12% increase) is not possible because some byproducts are always produced, the economic benefits through the production of cellulosic ethanol for a conventional fuel-ethanol plant are much greater than 12%.

Commercial technologies have been developed to optimize the conversion of corn-kernel fiber to ethanol, and they are currently available in three categories: (1) *in situ* technologies, in which fiber is converted to ethanol simultaneously with starch conversion, (2) technologies in which fiber is physically separated from other components of the corn kernel followed by processing of the fiber-rich material independently of the starch process train, and (3) technologies in which post-distillation residual solids from the conventional starch-based ethanol process provide the feedstock for conversion of the fiber fraction into ethanol.

In specific,

- Edeniq's *in situ* process is the most widespread due to the fact that no pretreatment is required and no additional capital investment is needed. It provides the lowest potential for increased ethanol yield
- ICM and Fluid Quip Process Technologies both provide fiber-separation technologies, which produce feedstocks with the highest concentration of corn kernel fiber (represent almost two-thirds of the dry mass), and produce beer with the highest potential concentration of ethanol. The costs associated with installing and operating the fiber-separation equipment, plus the costs associated with pretreatment, hydrolysis, fermentation, and ethanol recovery equipment, could post an additional barrier to implementing them in existing ethanol plants.
- Quad County Corn Processors and D3Max use post-distillation residual solids as the source of corn-kernel fiber, with Quad County using whole stillage and D3Max using wet cake. They both use dilute-acid pretreatment to achieve high conversion efficiency, and separate fermentation tanks for the cellulose- and hemicellulose-derived sugars in order to obtain the maximum possible increase in ethanol yield using genetically modified (GMO) yeast.

More detailed information about these commercial technologies are shown in Table 1.

Barriers to implementation of these technologies include the cost of installing the equipment needed to effectively convert the corn kernel fiber to ethanol, the limited availability of arabinose-fermenting yeast strains, and the relatively high cost of recovering CKF-derived ethanol by conventional distillation and dehydration technologies due to the low ethanol concentration that may be present in cellulosic beer.

Table 1. Summary of Commercial Technologies for Corn-Kernel Fiber Conversion

Company	Edeniq	ICM	Fluid Quip Process Technologies	Quad County Corn Processors	D3Max
Technology	Edeniq Intellulose	Selective Milling Technology™ (SMT V2™) Fiber Separation TechnologyTM (FST Next GenTM)	Selective Grind Technology™ (SGT ™) Fiber By-PassTM (FBPTM)	QCCP Technology	D3Max
Category	*in situ* process	Fiber-separation	Fiber-separation	Post-distillation residual solids (whole stillage)	Post-distillation residual solids (wet cake)
Contact information	2505 North Shirk Road Visalia, California 93291 (o) 559-302-1777	310 N. First Street Colwich, KS 67030-0397 (o) 316-796-0900	6105 Rockwell Dr. NE Cedar Rapids, IA 52402 (o) 319-320-7709	6059 159th St., Galva, IA 51020 (o) 712-282-4628	308 Second Ave. N., Suite 304 Grand Forks, ND 58203 (o) 866 746-8385
Stage of Commercia-lization	i. Six plants with EPA approval; ii. Three awaiting for approval; iii. Six preparing to gather data for their applications	A new plant being built in Colwich, KS (ELEMENT, LLC, a collaborative project involving ICM and The Andersons, Maumee, OH)	No public information	Only QCCP	Only Ace Ethanol
Conversion (starch ethanol)	Not applicable	Up to 3%	Up to 3%	Not applicable	Not applicable
Conversion (cellulosic ethanol)	Up to 2.5%	Not reported	Up to 4.5 - 8%	Up to 9%	Not reported

1. Introduction

Cellulosic biofuels are derived from structural carbohydrates (i.e., cellulose and hemicellulose) or lignin, and in order to qualify under the Renewable Fuel Standard (RFS), must result in a 60% reduction in greenhouse gas production relative to a 2005 baseline for petroleum fuels (U.S. EPA). For many popular cellulosic feedstocks, such as corn stover and switchgrass, new supply chains and processing facilities must be developed to effect their conversion into biofuels. Corn-kernel fiber (CKF) is a cellulosic feedstock that is already being harvested, stored, and transported to existing fuel-ethanol plants as a component of corn kernels, and therefore, conversion technologies may be rapidly commercialized due to the great economic benefits.

In a whole kernel corn, starch is the most abundant component and is the precursor for conventional fuel ethanol. Corn-kernel fiber represents about 8 to 9% of the dry mass of the kernel (Watson, 1987). About half of CKF (51%) is present in the pericarp (i.e., the hull) and the tip cap, and the rest is present in the walls of cells that are distributed throughout the endosperm (27%) and germ (16%) (Gulati *et al*., 1996). The pericarp and tip cap can be separated from the other components of the corn kernel relatively easily using conventional dry milling techniques, but the fiber that is present in cell walls requires more complex wet-milling operations. About one-third of CKF is cellulose, and almost two-thirds of the mass is hemicellulose (lignin represents less than 5% of CKF).

Cellulose, like starch, is a polymer that is composed exclusively of glucose. The difference between these two polysaccharides is the chemical bonds that connect glucose molecules to each other, and that differences are the ultimate cause of the physical and biochemical differences between starch and cellulose. CKF hemicellulose is highly branched and consists primarily of xylose (48 to 54%), arabinose (33 to 35%), galactose (5 to 11%), and glucuronic acid (3 to 6%). Galactose is fermentable by conventional yeast, and genetically modified yeast capable of fermenting xylose to ethanol are commercially available. Few arabinose-fermenting strains appear to be commercially available at this time, and glucuronic acid is not fermentable.

In general, a maximum of about 0.26 additional gallons of ethanol could be produced per bushel of corn by complete conversion of the cellulose-derived glucose and the hemicellulose-derived galactose and xylose that are present in corn-kernel fiber. This represents a potential increase of about 9% relative to the ethanol that could be produced by complete conversion of starch. Conversion of hemicellulose-derived arabinose would potentially add another 0.08 gallons of ethanol per bushel (i.e., an additional increase of almost 3% relative to starch-derived ethanol). Of course, complete conversion of these sugars to ethanol is not possible because some byproducts (e.g., glycerol, yeast biomass) are always produced, and 100% conversion of polysaccharides to fermentable sugars is difficult to achieve.

2. Operations and Processes for Production of Ethanol from Corn Kernel Fiber

Conversion of corn kernel fiber into biofuels and biochemicals usually involves a combination of physical and chemical operations and processes that convert cellulose and hemicellulose into fermentable sugars. Figure 1 is a block diagram showing the processes and operations that would be used to produce cellulosic ethanol.

Conversion usually starts with pretreatment, which typically involves high temperatures (e.g., 70 to 200 ^{o}C), high pressures (e.g., 15 to 400 psig), and relatively short reaction times (e.g.,

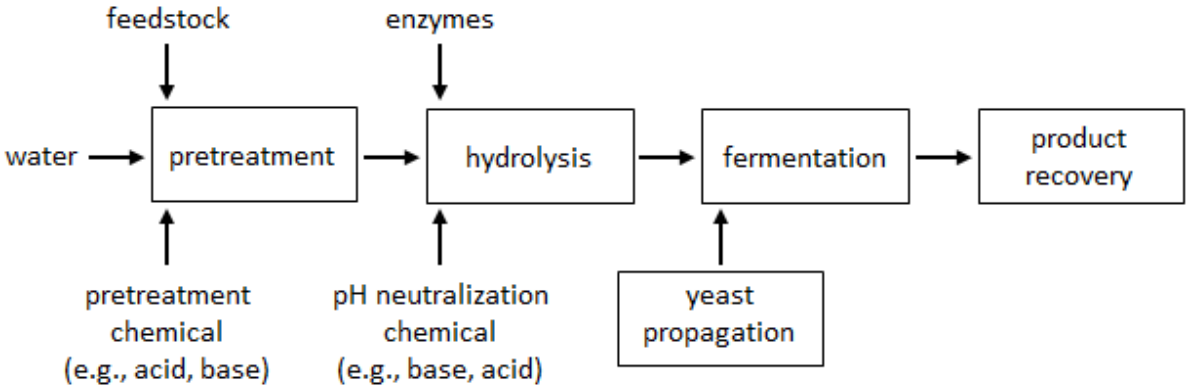

Figure 1: Typical processes and operations involved in conversion of cellulosic feedstocks to biofuels. Inputs shown below the processes and operations are optional.

10 minutes to about 1 hour). Pretreatment is required to disrupt the intermolecular interactions between cellulose, hemicellulose, and lignin that give cellulosic materials its structural strength (Saha et al., 1998; Mosier et al., 2005). Pretreatment may or may not involve use of a pretreatment chemical (e.g., dilute sulfuric acid, ammonia, lime), and some pretreatment conditions (e.g., acidic pretreatment) result in direct hydrolysis of hemicellulose. Operations that involve high pressures are followed by a flash tank, in which the pressure is rapidly reduced to near ambient, and the rapid depressurization may further disrupt the quasi-crystalline structure of cellulose. One pretreatment mechanism—steam explosion—is based on rapid depressurization and does not require the addition of a pretreatment chemical, but the temperatures (e.g., 210 to 250 ^{o}C) and pressures (e.g., 260 to 550 psig) involved in this operation are extremely high (Jeoh, 1998).

Hydrolysis is the process through which high molecular weight polysaccharides are converted into fermentable sugars: cellulose is converted to glucose, and hemicellulose is converted to xylose, galactose, and arabinose. The optimal conditions for cellulose hydrolysis by commercially available enzymes include pH from about 5 to 5.5 and temperature around 50 ^{o}C. Therefore, the pretreated feedstock must be cooled before entering the hydrolysis reactor, and if pretreatment was conducted at a pH that is significantly outside the optimal range, the pH must be adjusted. Typical reaction times for hydrolysis are on the order of a day or more to achieve maximal conversion of cellulose and hemicellulose to fermentable monomers.

After hydrolysis is complete, the temperature is reduced, and the hydrolysate is inoculated with yeast. Like hydrolysis, fermentation reaction times are typically on the order of a day or more. In some cases, hydrolysis and fermentation occur concurrently in the same tank. In this case, called simultaneous saccharification and fermentation (SSF), the reaction temperature is lower than the optimal temperature for the enzymatic reaction in order to make the process compatible with the temperature requirements for yeast growth, and therefore, the hydrolysis reaction proceeds much more slowly than it does at the optimal temperature. As described in the previous section, xylose and arabinose that are produced by hydrolysis of hemicellulose are not fermented by conventional yeast, and therefore, if they are to be converted into ethanol, the fermentor must be inoculated with genetically modified yeast, which must be propagated

separately from the conventional yeast used in starch fermentation. In some cases, the hydrolysate from the CKF cellulosic conversion process may be added back to the starch process train, and starch- and fiber-derived sugars may be fermented in the same tank. (Note, however, that most xylose-fermenting yeast cannot tolerate the ethanol concentrations that are achieved in the starch-based fermentations that are typical of the fuel-ethanol industry.)

Recovery of the product from cellulosic ethanol fermentations can use the same types of operations that are used to recover ethanol produced by fermentation of starch-based feedstocks, but the energy efficiency of these operations is strongly affected by product concentration (Vane, 2008): at low concentrations, as are sometimes produced by fermentation of corn kernel fiber, recovery of ethanol by distillation followed by molecular-sieve dehydration can be energy inefficient. Unfortunately, few commercially viable alternative technologies are available, and increasing the ethanol concentration of the fermentation broth to a point at which recovery by distillation becomes economically feasible may be the best approach.

3. Commercial Technologies for Conversion of Corn-Kernel Fiber

Commercial technologies for conversion of corn-kernel fiber to ethanol can be divided into three categories: (1) *in situ* technologies, in which fiber is converted to ethanol simultaneously with starch conversion, (2) technologies in which fiber is physically separated from other components of the corn kernel followed by processing of the fiber-rich material independently of the starch process train, and (3) technologies in which post-distillation residual solids from the conventional starch-based ethanol process provide the feedstock for conversion of the fiber fraction into ethanol.

In situ technologies have the advantage of simplicity because, in some implementations, they require no additional equipment beyond what is used by conventional starch-based ethanol plants. The disadvantage is that corn-kernel fiber, requires pretreatment to promote significant enzymatic conversion of cellulose and hemicellulose to fermentable sugars (Saha *et al*., 1998); so, the efficiency of these processes is likely to be low. Fiber-separation technologies involve the most additional equipment, but the products have high fiber concentrations. When fiber-rich feedstocks are pretreated, the concentration of fermentable sugars produced by hydrolysis can be relatively high, and therefore, the concentration of ethanol in the beer entering distillation may also be relatively high. Therefore, the unit costs of ethanol recovery may be relatively low for fiber-separation technologies. Additional equipment is not required to separate CKF from starch when post-distillation residual solids are used as the feedstock for cellulose pretreatment and hydrolysis, and the fraction of total CKF that is subjected to pretreatment and hydrolysis can be high (i.e., in some cases, 100% of CKF can be processed through the cellulosic pathway), but the concentration of cellulose- and hemicellulose-derived sugars in the hydrolysate may be relatively low unless the residual solids are concentrated before pretreatment. Commercial technologies that fall into each category are described in details in the white paper prepared by Wrenn and Zhang (2018).

4. Summary and Conclusions

Of the five commercial technologies that are currently available for converting corn-kernel fiber to fuel ethanol, Edeniq's *in situ* process is the most widespread (i.e., it is reportedly being used in 15 ethanol plants [Perkins, 2018] versus one or fewer plants that are known to be using the other technologies). The reason for its popularity is almost certainly due to its simplicity and its ability to be implemented without any additional capital investment. Because this process—as it is being implemented in most cases—does not include pretreatment, however, it also provides the lowest potential for increased ethanol yield: the maximum expected increase in ethanol production based upon complete conversion of CKF-derived C6 sugars (glucose and galactose) is 5% relative to what could be obtained from starch-derived sugars, and currently, only half or less of this potential is being achieved. Because xylose fermenters cannot tolerate the high ethanol concentrations that are achieved in typical starch-based fermentations, and xylose consumption by these strains is repressed by the presence of glucose, it may be difficult to improve the ethanol yield by using xylose-fermenting yeast strains.

Fiber-separation technologies (ICM and Fluid Quip Process Technologies) produce feedstocks with the highest concentration of cellulosic substrates. Whereas the concentrations of cellulose and hemicellulose represent only about one-third of the dry mass of whole stillage and wet cake, the total concentration of cellulosic polysaccharides in the fiber fraction produced by front- and back-end separation technologies may represent almost two-thirds of the dry mass (Wrenn and Zhang, 2018). All other things being equal, the ethanol concentration in the cellulosic beer should be proportional to the concentration of cellulosic polysaccharides entering the process train. So, fiber-separation technologies have the highest potential concentration of ethanol in the beer and, therefore, the lowest unit costs for ethanol recovery. Current materials-handling technologies limit the total solids concentration that can be used, however; so, this potential is probably not being realized at this time. The costs associated with installing and operating the fiber-separation equipment—over and above the costs associated with pretreatment, hydrolysis, fermentation, and ethanol recovery equipment—may represent an additional barrier to implementing these technologies in existing ethanol plants. As a result, fiber-separation technologies have not yet been installed in existing fuel-ethanol ethanol plants for the purpose of producing cellulosic ethanol from corn-kernel fiber.

The technologies that use post-distillation residual solids as the source of corn-kernel fiber (i.e., Quad County Corn Processors and D3Max) can be implemented in a relatively straightforward manner because conventional liquefaction and fermentation processes remove almost all of the starch before the cellulosic conversion process. Both of these technologies use dilute-acid pretreatment to hydrolyze hemicellulose and make cellulose more susceptible to enzymatic hydrolysis. So, high conversion efficiency can be expected for these technologies. Also, since both of these technologies include separate fermentation tanks for the cellulose- and hemicellulose-derived sugars, yeast strains capable of fermenting five- and six-carbon sugars can be used to obtain the maximum possible increase in ethanol yield. The concentration of ethanol that can be expected in the cellulosic beer is relatively low for the QCCP technology because it uses whole stillage, which has a low concentration of total solids of which only about one-third is potentially fermentable polysaccharides. The concentration of ethanol in the cellulosic beer produced by the D3Max technology may be significantly higher than the concentration in beer from the QCCP process because the total solids concentration of the feedstock may be much higher. Materials handling limitations currently restrict the feedstock concentration for the

D3Max process to about 25% (w/w), which is only about twice as high as the concentration of total solids in the QCCP process, but improved technology could potential increase the total solids concentration entering the D3Max process to about three times the concentration that enters the QCCP process, which would increase the ethanol concentration in beer by a similar amount. Because the energy needed to separate ethanol from water by distillation decreases as the ethanol concentration increases, the costs of recovering cellulosic ethanol may be much lower for the D3Max technology than for the QCCP technology.

Conversion of all of the potentially fermentable sugars present in the cellulose and hemicellulose components of corn-kernel fiber (i.e., cellulose-derived glucose and hemicellulose-derived galactose, xylose, and arabinose) has the potential to increase the ethanol yield from corn by almost 12%. Although several technologies have been commercialized for converting corn-kernel fiber to ethanol, with the exception of Edeniq's Intellulose technology, the fuel-ethanol industry has been slow to adopt them. Barriers to implementation of these technologies include the cost of installing the equipment needed to effectively convert the cellulosic polysaccharides to ethanol, the limited availability of arabinose-fermenting yeast strains, and the relatively high cost of recovering CKF-derived ethanol by conventional distillation and dehydration technologies due to the low ethanol concentration that may be present in cellulosic beer.

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