The U.S. corn ethanol industry: An overview of current technology and future prospects

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Abstract

Last year, 1.77 billion gallons of fuel ethanol were produced in the U.S., over 90% of which was produced from corn. Ethanol demand is expected to more than double in the next several years as it is used to replace the fuel oxygenate, methyl tertiary-butyl ether (MTBE). Corn is prepared for ethanol fermentation by either wet milling or dry grinding. Most newly constructed ethanol plants use dry grinding because of its lower capital costs. However, corn wet millers have also expanded production by adding on to existing plants. Current technology allows for 2.5 (wet milled) to 2.7 (dry grind) gal of ethanol per bushel of corn. An opportunity exists for increasing this yield by also converting the fibrous components of the corn kernel (i.e. pericarp and germ) to ethanol. Fermenting these non-starch fractions could increase the yield from a bushel of corn by a maximum of 10%. In this brief review, the economic and technical aspects of ethanol production will be explored as well as future prospects for increasing ethanol yield from corn by fermenting the non-starch fractions.

Introduction

The United States produced 1.77 billion gal of fuel ethanol (2001) and over 90% of it was produced from corn. U.S. ethanol production has expanded dramatically since 1980 (Fig. 1) and today utilizes over 5% of the corn crop. Ethanol production should continue to increase as individual States phase out the use of methyl tertiary butyl ether (MTBE) as a fuel oxygenate. The California Energy Commission has estimated that production capacity is expected to grow to more than 4 billion gals/yr by 2006 (MacDonald et al., 2001).

The growth in the use of fuel ethanol can be traced to environmental legislation and Federal and State economic incentives. In 1990, the Clean Air Act amendment was passed which required the use of oxygenated fuel and reformulated gasoline to reduce carbon monoxide emissions. The list of available fuel oxygenates are ethanol, MTBE, and ethyl tertiary butyl ether (ETBE). Several Midwest States mandate the use of ethanol. The Federal government has also encouraged the use of ethanol by exempting it from the federal gasoline excise tax. This tax exemption was set to expire in 2000, but has since been renewed until 2006. Several Midwestern States also introduced further financial incentives for ethanol. These incentives are designed to favor smaller ethanol plants, such as those built by farmer cooperatives. Typical is Minnesota's Tax incentive, which gives 20 cents per gal per year for 10 years for a maximum of 50 million gals per year. Many ethanol plants designed around this incentive have since expanded capacity.

Ethanol demand is expected to increase dramatically over the next several years because of environmental concerns associated with the use of MTBE. MTBE, which has leaked from gasoline storage tanks, has been discovered to be a major ground water contaminant and more resilient to microbial degradation than other common organic water pollutants (Anonymous, 1999). As a result of these findings, California and States located in Eastern United States have

Figure 1. Growth in U.S. ethanol production
indicated interest in phasing out MTBE. In June 2001, the Bush Administration refused California's request for a waiver of the oxygenate fuel requirement, thereby, forcing the use of ethanol if production of MTBE is stopped. The annual California ethanol market is expected to grow by 500 - 800 million gals (McDonald et al., 2001). A possible compromise has recently been worked out in the U.S. Senate. In the proposed National Energy Bill (currently in the U.S. Senate) the oxygenate requirement would be abolished and, instead, a renewable fuels standard established for promotion of ethanol (Brown, 2002). The bill specifies a target ethanol production goal of 5 billion gals/yr by 2012 (ibid).

Beyond its use as an oxygenate, proponents of the use of fuel ethanol cite the following benefits: reduces reliance on imported oil, lowers greenhouse gas emissions, and promotes rural development. A study to be published this spring (2002) by the USDA has estimated that ethanol has a 34% net energy balance (Shapouri personal communication, for an older report see Shapouri et al., 1995). Ethanol is available as a 10% v/v (E10) and 85% v/v (E85); only in the Midwest) blend with gasoline. E10 and E85 lower petroleum use by 6% and 74% per gallon, respectively (Wang et al., 1999). E10 also reduces greenhouse gas emissions by 1% and E85 by 34% (ibid). Finally, ethanol is good for rural development by supplying an important market for corn and providing jobs at rural locations.

Current ethanol production processes

Corn is processed to ethanol by either dry grinding or wet milling. Last year, for the first time, dry grinding production (55%) exceeded that of wet milling in the U.S. Growth of dry grind mill capacity has exceeded that of wet mills because dry grind mills have lower capital costs. Capital costs for dry grind mills have been estimated at $1.25-1.50 per gal. In recent times, no new wet mills have been built; instead producers have relied on expanding existing facilities. Descriptions of the dry grinding and wet milling processes follow.

Dry grind process

Sometimes the ethanol dry grind process is referred to as dry milling. Dry grind process, however, is the preferred term as it avoids confusion with dry milling corn for production of corn grits and flour. A schematic of a dry grinding process is shown in Figure 2 (for detailed reviews: Jacques et al., 1999; Elander and Putsche, 1996). Corn is hammer milled to pass through a 1/8-3/16 inch screen. If the grits exit the mill too coarse, not all of the starch becomes available for fermentation and if it is too fine, the residual biomass is difficult to separate following fermentation.

Once ground, the corn is mixed with water to form a mash. The pH of the mash is adjusted to 6.0 with ammonia followed by addition of 1/3 of the alpha-amylose. Alpha amylase is added to begin to break down the starch polymer and produce soluble dextrins. The mash is heated to above 110°C using a jet cooker. The jet cooker is a special tube reactor/pump that uses direct steam heating to heat and shear the starch granules. The corn mash is kept at the elevated temperature for several minutes by pumping it through a holding tube equipped with a backpressure valve. The mash flows from the holding tube into a flash tank and the temperature is allowed to fall to 80-90°C. The rest of the alpha amylase is added and the mash is liquefied for at least 30 minutes. Liquefaction greatly reduces the size of the starch polymer.

The liquefied mash is placed in the bioreactor and cooled to 32°C. The pH is lowered to 4.5-5.0 using backpack (recycled from the distillation column) and phosphoric acid. The fermentation stage is started by adding the glucoamylase and the yeast inoculum. Glucoamylase converts liquefied starch into glucose by breaking down alpha-1,4 glucosidic linkages. Enough glucoamylase is added such that the saccharification of the starch to glucose, which occurs continually through the fermentation, does not limit the rate of ethanol production. In addition, either (NH₄)₂SO₄ or urea is added as a nitrogen source for the growth of the yeast. Recently, ethanol dry grind mills have also begun to add proteases that break down the corn protein to a free amino acid, which serve as an additional source of nitrogen for the yeast. The fermentation lasts 48-72 hours and has a final ethanol concentration of 10-12% v/v. The pH of the beer declines during the fermentation to below 4 because of carbon dioxide formed during the ethanol fermentation. The decrease in pH is important for increasing the activity of glucoamylase and inhibiting the growth of contaminating bacteria.

Dry grind plants can reduce the amount of glucoamylase added by saccharifying the liquefied starch at 65°C prior to fermentation. However, plants have gone to SSF (simultaneous saccharification and fermentation) because it lowers the opportunity for microbial contamination. SSF also lowers the initial osmotic stress...
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Upon completion, the beer is first distilled through the beer column. The distillate is further concentrated to 95% v/v of ethanol, at which concentration water and ethanol form an azeotrope. The ethanol is brought up to 100% v/v concentration using a molecular sieve bed. Finally, the ethanol is denatured with the addition of fusel oil, higher alcohols produced by the yeast during fermentation, and gasoline. Denaturation is required to avoid the alcohol beverage tax.

The stillage leaving the beer column is centrifuged with a decanter. Between 15 and 30% of the liquid fraction (thin stillage) is recycled as backset. The reminder is concentrated further by evaporation and mixed with the residual solids from the fermentation. The mixture is then dried to 9% moisture in a gas-fired rotary dryer. The final product is marketed as Distiller Dried Grains with Solubles. DDGS, ethanol and (for some plants) CO₂ are the only products (Table 1).

Wet milling process

Wet mill plants are larger and produce more products than dry grind plants (Table 1; for detailed reviews: Jacques et al., 1999; May 1987). Wet mills separate each component of the corn kernel: the endosperm, germ, and pericarp (e.g., corn hull). The endosperm is further separated into starch and gluten (protein) streams. The gluten is marketed as gluten meal; a high protein (60%) animal feed used mainly by the poultry industry. Corn oil is extracted from the germ. The pericarp is separated as corn fiber. The corn fiber is combined with the steep liquor and de-oiled germ meal and sold as corn gluten feed, a low protein (20%) animal feed. In addition to producing ethanol, most corn wet millers produce other products from the starch using either enzymatic or fermentation processes. Examples of these products are dextrin, high fructose corn syrup (HFCS), citric acid, amino acids, and lactic acid.

The key to isolating these different corn fractions is steeping (Fig. 3). In the steeping step, the corn is soaked in water and treated with SO₂ (1600 ppm) at 52°C for 20-40 hr. The corn is further acidified by the growth of lactic acid bacteria at later stages during the steep. Steeping swells the kernel and loosens the bonds between the protein and starch in the endosperm. Following steeping, the kernels are shredded in a mill designed to dislodge the germ. The germ, which contains about 30% oil, is then separated based upon its lower density compared to the rest of the kernel with hydrocyclones. The recovered germ is next processed to extract the corn oil, and the residual germ meal is blended into corn gluten feed.

The protein and starch are next separated from the fiber by passing the slurry along metal screens. The fiber is retained on the screens, while the protein and starch pass on. The recovered starch is further washed to remove residual protein. The cleaned starch, if used for ethanol or HFCS production, is enzymatically hydrolyzed to glucose using alpha amylose followed by glucoamylase. As
with dry grinding, a jet cooker is used during the liquefaction step. Separate saccharification and fermentations steps are carried out. To aid in saccharification, pullulanase is added with the glucoamylase. The fermentation is carried out in a laboratory. The results have shown that hybrids with similar starch contents can still vary in extractable starch contents (Zehr et al., 1995). The superior hybrids are rated for high extractable starch content.

**Modified milling processes**

Modified milling processes have been demonstrated in the laboratory that allow for recovery of germ and pericarp fractions. By allowing the gluten to remain with the starch, steeping times can be greatly reduced and SO2 eliminated (Singh and Eckhoff, 1996). The corn is soaked (31% solids loading) for 12 hr in 0.5% lactic acid at 59°C followed by milling to release the germ (Singh and Eckhoff, 1996). The germ is separated in a germ cyclone. Fiber is either recovered with the germ by adjusting the density of the slurry through the cyclone or after germ collection by re-adjusting the slurry density and passing it through an additional cyclone (Wahjudi et al., 2000). Removal of the germ and fiber allows for collection of corn oil and increased ethanol productivity (per bioreactor volume) because the fiber load is reduced from 18 to either 14 or 10% (dw/dw) (Taylor et al., 2001). Capital costs for a 31 million gal ethanol/yr using the Quick Fiber process are forty-nine million U.S. dollars. A comparable dry grind plant is estimated to cost thirty-eight million dollars (Singh et al., 2001). For crude corn oil selling at $0.55/kg, an additional $0.01 per litre can be realized in net additional income for the Quick Fiber vs. conventional dry grinding (Taylor et al., 2001).

**Lignocellulosic biomass conversion**

Approximately 11% of the carbohydrates present in corn are not in the form of starch. These fractions consist of cellulose and xylan present in the hull (i.e., pericarp) and germ meal, and are folded in the corn gluten feed (wet milling) and DDGS (dry grinding). Removing part of the fiber from the feed co-products would increase their relative protein contents and, therefore, their value on a weight basis. These feedstocks are also, conveniently located at ethanol plants. The amount of ethanol that could be produced is significant (Table 2). However, DDG contains considerable quantities of yeast, which might interfere with pretreating it for fermentation. Conversion to a modified dry grind mill would allow for collection of the fibrous fractions prior to starch fermentation. In addition to the fibrous component of the kernel, the rest of the corn plant (e.g., corn stover) could also serve as a feedstock for ethanol. Corn stover contains 58% carbohydrates (Table 2) and 1.0-1.5 lb of stover is produced per lb of harvested corn (Wiselogel et al., 1998). Unlike DDG and corn fiber, collecting and storing corn stover represents a formidable

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### Table 1. Corn milling product yields and selling prices

<table>
<thead>
<tr>
<th>Co-Product</th>
<th>Yield (per bushel)</th>
<th>Selling Price (U.S. $)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Corn Dry Grind Ethanol Fermentation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>16.7 lb</td>
<td>na</td>
</tr>
<tr>
<td>DDGS</td>
<td>16 lb</td>
<td>82 per ton²</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.65 gal</td>
<td>1.40-1.50 per gal³</td>
</tr>
<tr>
<td><strong>Corn Wet Milling Ethanol Fermentation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>15.8 lb</td>
<td>na</td>
</tr>
<tr>
<td>Corn Oil</td>
<td>1.83 lb</td>
<td>0.182 per lb³</td>
</tr>
<tr>
<td>Corn Gluten Meal</td>
<td>2.60 lb</td>
<td>217 per ton²</td>
</tr>
<tr>
<td>Corn Gluten Feed</td>
<td>11.2 lb</td>
<td>57 per ton²</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.50 gal</td>
<td>1.40-1.50 per gal³</td>
</tr>
</tbody>
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1 Distillers dried grains with solubles
2 Feedstuff, March 18, 2002 (Chicago prices)
3 Chemical Market Reporter March 11, 2002 (Midwest Prices)

### Table 2. Potential ethanol production from corn fibrous fractions

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Carbohydrate (% wt/wt)</th>
<th>Starch (% wt/wt)</th>
<th>Cellulose (% wt/wt)</th>
<th>Xylan (% wt/wt)</th>
<th>Availability (tons per yr)</th>
<th>Ethanol¹ (gal per yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Stover</td>
<td>58.4</td>
<td>–</td>
<td>36.4</td>
<td>22</td>
<td>125-200×10⁵</td>
<td>7.5-12×10⁶</td>
</tr>
<tr>
<td>Corn Fiber</td>
<td>69.6</td>
<td>19.7</td>
<td>14.1</td>
<td>32.4</td>
<td>3.4×10⁶</td>
<td>385×10⁶</td>
</tr>
<tr>
<td>DDGS</td>
<td>46.5</td>
<td>–</td>
<td>22.8</td>
<td>20.7</td>
<td>3.0×10⁶</td>
<td>133×10⁶</td>
</tr>
</tbody>
</table>

¹ Assumes theoretical ethanol yield
² Compositional Data: Corn Stover (Wiselogel et al., 1996), corn fiber (Grohmann et al., 1997), DDGS (Miron et al., 2001). Availability Data: Corn Stover (Glassner et al., 1998), Corn Fiber (Anonymous, 2000), DDGS (estimated from U.S. Renewable Fuel Association ethanol data, 2001)
³ Availability includes all wet milled corn
making the cellulose fraction susceptible to enzymatic hydrolysis by cellulase. Inhibitors are formed by subsequent degradation of sugars freed during hydrolysis, releasing organic acid side-groups (e.g., acetate) from the xylan component, and also from lignin break down products. Conditions that optimize cellulose recovery tend to also favor degradation of the xylose sugars and, therefore, optimal pretreatment conditions require a compromise. A wide variety of pretreatments have been investigated for biomass, and the best pretreatment, as expected, depends upon the source of biomass.

Most pretreatments are either chemical or a combination of chemical and physical (for review: Hsu T.A., 1996). Pretreatments described in the literature include: dilute acid, strong acid, alkaline hydrogen peroxide, ammonium fiber explosion (AFEX), steam explosion with SO₂, and hot water. Pretreating with acid is capable of completely hydrolyzing the xylan fraction. Alkali and hot water methods will only dissolve and partially hydrolyze xylan. This means hydrolysis will need to be completed using either enzymes or acid. Steam explosion tends to be more destructive to pentose sugars than some of the other methods. Acid pretreatments are the only ones that have been used commercially. For efficient recovery of the xylose sugars, the cellulose fraction needs to be hydrolyzed in a separate step.

Hydrolysis of the cellulose fraction, to release glucose, can be accomplished enzymatically or chemically. Acid hydrolysis, under sufficiently harsh conditions, can completely hydrolyze cellulose to glucose. However, these harsh conditions lead to the formation of inhibitors and, so, in the literature enzymatic digestion has been favored. Often, the cellulase enzymes are added to the fermentation broth and carried out as a simultaneous saccharification and fermentation. Carrying out hydrolysis during the fermentation lowers the amount of enzyme required and circumvents the sensitivity of the cellulase enzymes to end product inhibition. Even when the best treatment for pre-treating cellulose is used, cellulase loading is much higher than that needed for amylases. Thus, the cost of cellulases is considered a major technical constraint to implementing biomass fermentations.

Corn fiber, corn bran, and corn germ meal are readily hydrolyzed with dilute acid (Asghari et al., 1996, Dien et al., 1999, Grohmann and Bothast, 1997, Saha and Bothast, 1999). Dilute sulfuric acid hydrolysis of corn fiber at 140–160°C and pH 1.5–2.0 for 10-30 min followed by enzymatic saccharification of dextrans gave a yield of 81-87% of total carbohydrates as free sugars (Grohmann and Bothast, 1997). Only 7 international filter paper units of cellulase per g corn fiber cellulose were required, which is 2.7 times less activity than usually added to dilute acid pretreated cellulose (ibid). Other pretreatments used with corn fiber (AFEX, alkaline peroxide, and hot water), while effectively preparing cellulose for enzymatic treatment, do not completely hydrolyze the xylan (Weil et al., 1998, Moniruzzaman et al., 1997, Leathers and Gupta, 1996). Hydrolysis of AFEX treated corn fiber xylan with commercial xylanases only converted 25% to monosaccharides (Hespell et al., 1997). Corn germ xylan was more readily digested (ibid). The relative digestibility of hot water treated corn fiber xylan has not yet been reported. The AFEX and hot water treatments are still of interest because they do not generate gypsum waste, which is associated with neutralization of the dilute-acid treated biomass, and have lower concentrations of microbial inhibitors.
What's on Your Mind?

March on the Sugar Technology Forum

March on the Sugar Technology forum was much quieter than the first months of the year, perhaps members had exhausted themselves reading and writing! Just under 50 messages were posted and, as there are always topics being discussed, some topics were carried over from February.

There was no clear leader this month and no particular sector of the industry stood out although it was good to see at least two topics – alcohol production and cossette handling – which were quite focused. In general, many of the topics discussed are common to both beet and cane [the process house and beyond in particular] and hence are relevant to more members but this should not stop you from asking or commenting on subjects related to just one sector.

One of the ongoing topics was the question of molasses exhaustion. It is no wonder that such an important subject should receive attention, giving less experienced members to improve their overall recoveries. Another of the topics from previous months was more of a flash-back as information which had been requested several weeks before if the topic was to be fully understood finally became available. The question related to flue gas energy losses up the stack, another important efficiency parameter which many people do not appreciate.

One of the key new questions earlier in March was the question of product sugar specification. It is clear that ‘brown sugar’ cannot really be specified and that ‘white sugar’ specifications vary around the world, usually with several different specifications covering different ranges of parameters applying for different uses.

Later in the month the question which stood out was how to split cossettes [the name given to the slices of beet prepared for extraction] between two extraction lines. The question came from a member faced with solving the problem for an expansion project and the assistance provided was both professional and prompt. We are looking forward to hearing of success in the future.

It is now almost a year since the forum was set up on Yahoo! and long-standing members will recall the reasons for doing so as the previous host staggered along. There is no doubt that the split left many people confused and, although necessary at the time, was not for the ultimate good of the industry and its technologists. We are therefore currently talking to see whether a merger cannot be achieved and hope to have more news soon.

If you want to know more then the forum web address is <http://groups.yahoo.com/group/sugartech> and you can join the forum at <www.sucrose.com/forum>
Fermentation of the sugars recovered from the xylan fraction is problematic because the traditional yeast, *S. cerevisiae*, does not ferment pentoses. Naturally occurring yeast that do ferment xylose require aeration for growth, have low productivity, are acutely sensitive to inhibitors - especially acetic acid, and have fairly low ethanol tolerances. There are no commercially suitable naturally occurring bacteria or yeast for fermenting xylose to ethanol (Bothast et al., 1999). Therefore, research has focused upon developing recombinant organisms to ferment pentoses to ethanol. Two strategies have been used to develop the needed biocatalyst: (1) expressing genes needed for xylose utilization in efficient ethanol producing microorganisms or (2) expressing genes needed for ethanol production in bacteria capable of using xylose and arabinose. As examples of the first approach, *Saccharomyces sp.* (Hahn-Hägerdal et al., 2001; Ho et al., 1998) and multiple *Zymomonas mobilis* strains (Zhang et al., 1995) have been constructed that ferment xylose. Examples of the second approach are ethanologenic *E. coli* strains (Dien et al., 1999, Ingram et al., 1998, Ohta et al., 1991). Several of these recombinant organisms have been used to ferment corn fiber hydrolysate (Table 3; Bothast et al., 1999). Of those listed in Table 3, only the *K. oxytoca* and *E. coli* are capable of fermenting arabinose. Arabinan represents 3.5%-5% of the total carbohydrates of corn stover (Wiselogel et al., 1996) and 16% of that for corn fiber (Grohmann and Bothast, 1997).

A scalable process for converting corn fiber to ethanol has been demonstrated by the authors (Dien et al., 1999). Specifically, the xylan portion was fermented, which left the cellulose fiber available for use in animal feed. The corn fiber was mixed with dilute acid (1.1% v/v sulfuric acid) to form a 17% (dry wt/total wt) solids loading. The mixture was pumped into a reactor vessel equipped with an external jet siphon mixer and a steam jacket. The slurry entered the reactor through the jet siphon, which allows for direct steam heating. The corn fiber was held in the tank for 15 minutes at 145°C. The liquid portion was recovered for fermentation. The hydrolysate syrup contained a total of 76 g/litre of sugars, which is 95% of theoretical, excluding cellulose. The corn fiber hydrolysate was next overlimed to remove inhibitors. This process consists of adjusting the pH to 10 with Ca(OH)₂ and treating the hydrolysate to 90°C for 30 minutes. The hydrolysate was neutralized with sulfuric acid to pH 7 and the resulting gypsum formed and removed by centrifugation. Yeast extract and tryptone were added as nitrogen sources. The hydrolysates were fermented using an ethanologenic *E. coli* strain. The fermentation was completed within approximately 65 hours and the ethanol yield was 92% of theoretical. Residual xylose was 3.5 g/litre.

Even if ethanol production is increased to 5 billion gallons per year in 2012, as being considered by the U.S. Congress, fuel ethanol would only displace 3.05% of the U.S. projected automotive fuel demand. Increasing ethanol supplies to greater production levels will eventually require fermenting lignocellulosic biomass (e.g. corn stover). Likewise, even though corn hulls and germ contain lignocellulose, they are also in limited supply as an ethanol feedstock. However, fermentation of these fibrous material can act as a stepping stone towards development of other, more challenging source so biomass, such as corn stover.

### References


La industria del etanol de maíz en los Estados Unidos: Una visión global de la tecnología actual y las perspectivas de futuro

Resumen

El año pasado, se produjeron en los Estados Unidos, 1,77 billones de galones de etanol combustible, más del 90% del cual proviene del maíz. Se estima que la demanda de etanol llegará a más del doble en los próximos años ya que es utilizado para reemplazar el combustible oxigenado: metil ter-butil-eter (MTBE). Para la fermentación de etanol, el maíz se prepara ya sea por molienda húmeda o triturando a seco. La mayoría de las nuevas plantas de etanol utilizan molienda en seco ya que las inversiones de capital son más bajas. No obstante, los molineros de maíz en húmedo han expandido la producción agregando sobre plantas existentes. La tecnología actual da lugar a 2,5 (molienda húmeda) o 2,7 (molienda seca) galones de etanol por bushel de maíz. Es posible incrementar este rendimiento si los componentes fibrosos del grano de maíz (por ejemplo el pericarpio y germen) también son convertidos a etanol. La fermentación de estas fracciones no amiláceas podría aumentar el rendimiento de un bushel de maíz en un máximo de 10%. En esta sección breve se exploran los aspectos técnicos y económicos de la producción de etanol, y también las perspectivas futuras para incrementar el rendimiento de etanol de maíz mediante la fermentación de las fracciones no amiláceas.