

Fuel ethanol production

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History

Motor fuel grade ethanol (MFGE) is the fastest growing market for ethanol worldwide; and MFGE production dwarfs the combined total production of all other grades of ethanol. Fermentation ethanol, as fuel (and solvent), has experienced several cycles of growth and decline since the early 1800s. By 1860, production had reached more than 90 million gallons per year. In 1861 Congress imposed a tax of \$2.08 per gallon. About that time, oil was found in Pennsylvania. Thus began the cycle of 'control' of fuel ethanol markets (and therefore production) by taxation policy and oil industry influence on government. Petroleum interests dominated the world fuel industry in the post-World War II era, until a major policy shift by Brazil in the 1970s led to an ethanol-fueled motor vehicle strategy, followed a decade later by the US (Morris, 1994, personal communication). As a result, the combined motor fuel ethanol production from fermentation in the Western Hemisphere exceeded 5.5 billion gallons per year in 2002.

In Central and South America the dominant MFGE feedstock is sugar, either in the form of cane juice directly from crushed cane (autonomous distilleries), or from molasses (annexed distilleries). In North America, the dominant feedstock is starch from grain, with 90% derived from corn. Feedstock choice

follows regional dominant agricultural output (Katzen, 1987).

Since the technology for producing MFGE from sugar sources is an abbreviated form of ethanol production from starch, which is in turn an abbreviated form of production from whole grain, this chapter will focus on MFGE production from whole grain as typically practiced in North America. This technology is generally known as dry milling (Raphael Katzen Associates, 1978).

Introduction

A comparative evaluation of potable ethanol and MFGE production processes reveals many similarities. As the MFGE industry began to develop, it looked to the distilled spirits industry for technology. In the US, many early MFGE plants copied beverage alcohol distillery processes, differing primarily in the addition of dehydration facilities copied from the industrial-grade ethanol industry (Madson and Murtagh, 1991). This generally ensured a plant capable of producing ethanol. This technology strategy, coupled with a strong ethanol market during the 1980s, often resulted in positive cash flows.

This technology strategy continued until a downward trend in ethanol pricing revealed the

critical difference between distillery and MFGE economics. Distilleries are traditionally operated for consistency in flavor and quality of product. Other factors such as yield, energy efficiency, labor cost, etc., while being important, did not dominate the economics. For the beverage distiller it is counterproductive to reduce cost of production at the expense of flavor and quality and, possibly, market share. Flavor and product consistency are so important that any benefit associated with a process change must be extremely high to offset the inherent market risk, which could be catastrophic if the product must be aged for several years. This, combined with the price differential between distilled potable spirits and MFGE, caused a shift to new technology development and differentiation of the MFGE industry in order to survive periods of high grain cost and low MFGE prices.

The MFGE producer has minimum product quality-related constraints. MFGE specifications for water content, acidity, solids, etc. (as defined in ASTM D-4806) can be met while concurrently minimizing operating costs. MFGE producers have traditionally operated with narrow profit margins. The drop in ethanol price during the mid 1980s resulted in most of the beverage distillery technology-based MFGE producers ceasing operations. Many of these operations were labor- and energy-intensive and operated with poor yields (Madson, 1990).

The design of a successful MFGE facility requires a clear understanding of the economic sensitivities. Evaluation of dry milling operating costs revealed that feedstock costs comprise over 60% of the total (Hill *et al.*, 1986). Energy consumption, at one time the central focus of debate, has been reduced via a rapid development of technology to less than 40,000 BTUs per gallon of product, which is approaching the point of diminishing returns in cost trade-offs (Hill, 1991; personal communication). The key issues today are feedstock conversion efficiency, capital investment, environmental impact and user-friendliness.

Conversion efficiency (yield)

Most MFGE producers have little control over feedstock pricing beyond hedging strategies

such as trading in futures. The producers' primary edge is therefore to maximize yield. Prior to the major growth of the MFGE industry, the typical yield in the production of spirits and industrial ethanol was five proof US gallons per distiller's bushel (56 lbs) equivalent to 2.375 undenatured gallons per bushel in MFGE terms. By the early 1980s, the newly-developed MFGE technologies had demonstrated (in top-performing plants) achievements of 2.55 undenatured US gallons per distiller's bushel (gpb) in dry milling plants and 2.45 gpb in wet milling plants. More recently, some dry milling MFGE plants have achieved sustained yields of 2.8 gpb (undenatured basis).

Because of the different industry reporting procedures, this discussion is based on the 'pay-to-pay' analysis. That is, yields are presented on the basis of unadjusted distiller's bushels of grain purchased and ethanol sold (undenatured basis) over a time period exceeding three months. This results in a market-based yield figure that refers directly to profit.

What brought about this remarkable yield increase? The major development in technology has occurred in the dry milling industry, primarily because of the variety of technologies tested and the broad-based experience from which to learn (Katzen *et al.*, 1992).

Beginning with the cooking step, it has become clear that the controlling factor in design of a cooking system is *not* the cooking of starch, but rather elimination of bacteria in order to achieve and maintain sterility throughout the process (Kemmerling, 1989). Because conditions needed to achieve sterility are different from conditions required to cook starch, other factors must be considered. Cooking must be conducted with minimum solubilization of potential fermentables in order to minimize adverse reactivity; yet all fermentables must be released during the liquefaction, saccharification and fermentation processes for complete conversion to ethanol. This includes the fermentable sugars embedded in the fiber matrix. Premature solubilization of potential fermentables risks side reactions that can result in unfermentable starch and sugar complexes because of high temperature and the presence of water and other reactive components. These reactions may be as simple as retrogradation of starch or as complex as reactions between amino

acids and carbohydrates. An example of a mashing and cooking system that has demonstrated maximum yield is illustrated in Figure 1.

Competing ‘cooking’ factors can be balanced by selecting a grind that allows minimum mobility of the sugars and starch within the grain particle matrix, yet provides necessary hydration. This is followed by instantaneous ‘jet cooking’ in the absence of adverse catalysts. By proper design of the cooking flash-down to liquefaction temperature (including valve selection), the ‘locked in’ fermentables can be released for full access by liquefying and saccharifying enzymes. Further, the non-starch fermentables are released from the fiber matrix to become available to the yeast. By keeping the fermentables ‘locked in’ within the particle matrix until the liquefaction tank has been reached, maximum retention and availability of fermentable value is achieved.

The next critical step is liquefaction. By liquefying to minimum dextrose equivalence (DE) at high temperatures for short time periods, adverse reaction conditions that convert fermentables to non-fermentables are minimized. Little of the starch is converted, and is therefore protected from adverse reaction until fermentation conditions are reached.

The key to creating maximum availability of fermentable carbohydrates is to reach the outlet

of the mash cooler with virtually sterile mash while providing minimum exposure of carbohydrate to adverse reactions. At the same time, the system must maximize downstream availability of fermentable carbohydrate embedded in the fiber matrix. Upon reaching the fermentation temperature, undesirable side-reactions in the mixture are minimal.

From the mash cooler forward, yield is strictly a function of enzymatic hydrolysis, fermentation technology, sterility and completion. High sustained yields, above 2.75 gpb (2.9 gpb as denatured MFG product), have been achieved with simultaneous saccharification and fermentation (SSF). SSF technology was developed in the 1970s to solve a fundamental problem in the conversion of cellulose to ethanol. The MFG industry has advanced this technology to provide even higher yields by incorporating simultaneous yeast propagation (from active dry yeast) in the fermentor during initial saccharification. Thus, SSYPF (simultaneous saccharification, yeast propagation and fermentation) has become the low-cost, high-yielding technology of choice (Figure 2). Significant sugar concentrations do not develop in the fermentor, thus avoiding sugar inhibition of both enzymatic hydrolysis and yeast metabolism. As a further consequence, bacterial growth is inhibited due to lack of free sugar substrate. Sugars are converted by yeast to

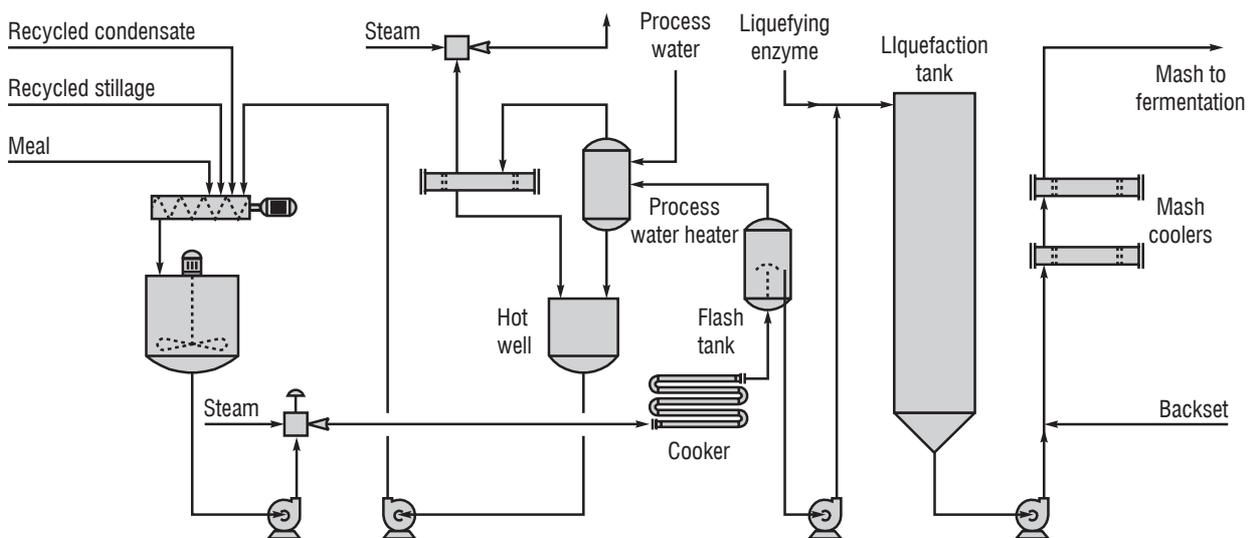


Figure 1. Mashing and cooking.

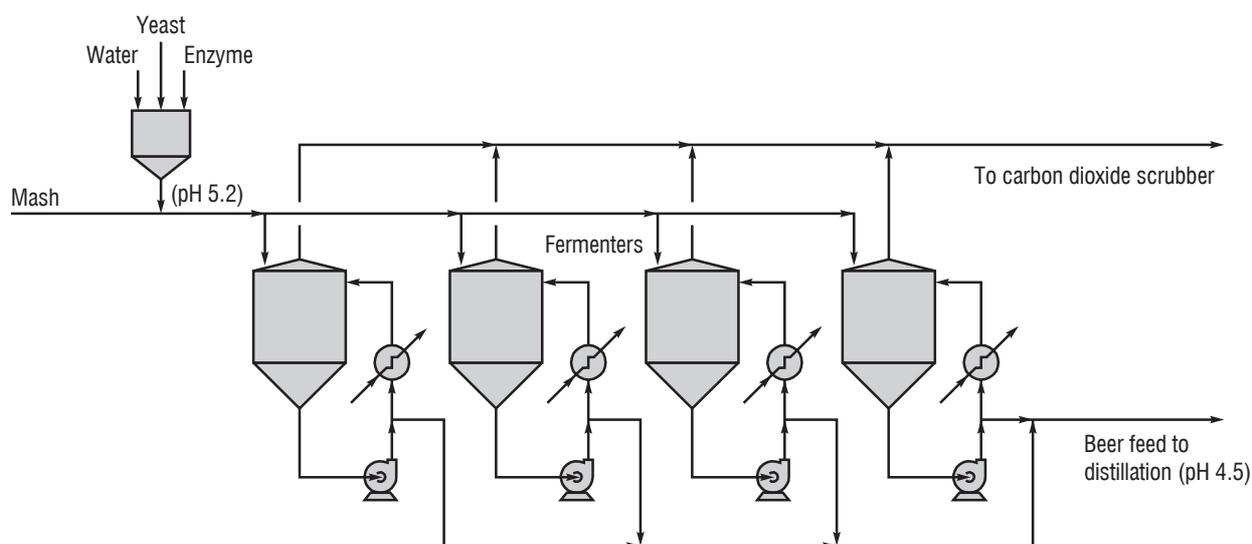


Figure 2. Simultaneous saccharification, yeast propagation and fermentation (SSYPF).

ethanol as rapidly as they are produced. By proper maintenance of pH, nutrients and sterility, full conversion of available starch and sugars to ethanol is achieved. Any pH excursions below 4.2 at the end of fermentation correlate directly with losses in yield (Bowman and Geiger, 1984).

This high-yield SSYPF technology has been employed in four plants in North America for which long-term technical results have been reported (Katzen and Madson, 1991). South Point Ethanol of South Point, Ohio (64+ million gallons per year undenatured MFGE) was the first plant known to have achieved the 2.75 gpb sustained yield milestone with corn feedstock for more than one year of operation (Hill, 1991; personal communication). Reeve Agri-Energy Corporation of Garden City, Kansas, operates an 11 million gallons per year plant with yields from milo and corn feedstock exceeding 2.75 gpb (Reeve and Conway, 1998; personal communication). Pound-Maker Agventures LTD of Saskatchewan, Canada, using wheat as feedstock, has achieved sustained yields equivalent to those of South Point Ethanol and Reeve Agri-Energy on a raw material starch and sugar basis (Wildeman and McCubbing, 1997; personal communication). More recently, Minnesota Energy Cooperative of Buffalo Lake, MN, in a plant now producing 18 million gallons per year, has achieved sustained yields of 2.8 gallons of MFGE per bushel of corn (Robideaux and Johansen, 1999; personal communication). On a 'product sold' basis, this yield is 2.95

gallons of denatured MFGE per bushel.

It has been suggested that lower yields result in increased animal feed co-product production; and since the market price of the co-product, distillers dried grains with solubles (DDGS), is generally greater than that of grain (per unit of weight), the production facility generates DDGS revenue to offset the losses in ethanol revenue. However, several issues need to be considered:

1. Every pound of starch or sugar not converted to ethanol must remain as starch, sugar, or be converted to a compound that does not involve the production of CO₂ (or other volatile by-product) in the requisite metabolic pathways. If not, production of one pound of DDGS will require consumption of two pounds of sugar, thereby negating the revenue trade-off.
2. If sugar or products of high-yield stoichiometric reactions pass directly through to DDGS, the soluble solids are recovered. Frequently, however, this results in complications in evaporator and dryer operations due to carbohydrate fouling and excess solubles syrup production. This can necessitate disposal of concentrated solubles syrup at significantly less than DDGS solids equivalent pricing. It can also result in a temporary decrease in production rate or may cause shutdown for cleaning.

3. Most plants are limited in centrifugation, evaporation or dryhouse capacity because these systems are the least productive from a return-on-investment perspective. Therefore higher ethanol yields maximize both plant production and productivity of the investment, since lower co-product production reduces demand on associated processing equipment.
4. For a plant of a given production capacity, increasing yield reduces the required size of most process equipment, with a corresponding decrease in capital investment. Higher yield, therefore, reduces debt service per unit of production.

What is this yield worth? If corn is priced at \$2.50 per bushel, DDGS at \$120.00 per ton and ethanol at \$1.12 per undenatured gallon, the net result of a yield increase from 2.5 to 2.75 gpb is \$0.145 per purchased bushel of grain (\$0.053 per gallon of ethanol) in additional profit. This profit gain is after deduction of the \$0.135 per bushel decrease in DDGS sales owing to reduction in carbohydrate pass-through to DDGS. Actual profit, however, will exceed \$0.145 per bushel due to the efficiency value of increased production with no increase in fixed cost and little increase in variable cost.

What does it cost to achieve these yields? Fortunately, the investment and operating costs associated with this high-yield technology are lower than those of the common technologies available in the 1970s and early 1980s. High-yield milling, mashing, cooking, liquefaction and SSYPF technology represents one of those pleasant, but rare, situations in which it costs less to get more.

As the result of this extraordinary advance, more than 90% of grain dry milling MFGE plants operating in 2002 in North America have adopted SSF, SSYPF or a similar fermenting process. Further, more than 90% of plants under construction have chosen this simultaneous technology (Tetarenko, 2002; personal communication).

Cascade fermentation

Although there are substantial variations in the

fermentation technologies applied in grain or starch conversion to ethanol, current operations can be described on a general basis. The broad divisions of technology are wet milling and dry milling. In wet milling, the major objective is to separate corn into a number of products such as starch, gluten, germ meal, germ oil, animal feed residue (gluten feed), dextrose, fructose, modified starches and a variety of specialty products. Production of MFGE from the lower grades of starch, or from all of the starch in an MFGE-dedicated plant, is an established conversion process in which starch slurry is cooked, liquefied and saccharified prior to fermentation.

All fermentation systems in use today are continuous with respect to input and output. Fermentation of saccharified starch in the wet milling process is carried out by either simultaneous (SSF or SSYPF) or cascade processes. Figure 3 shows a typical system for cascaded saccharification and yeast propagation. Figure 4 shows the continuation of the cascade with pre-fermentation and fermentation. This cascade technology has been applied successfully to wet-milled starch feedstock. Application to whole corn dry milling operations has been carried out on a large scale, but has not yielded results comparable to SSYPF technology.

Not only is less equipment required for SSYPF operation in dry milling plants, but the external saccharification step of cascade systems, a major source of infections, is eliminated. Also, SSYPF, which starts at pH 5.2 and ends at pH 4.5, may be carried out in carbon steel fermentors. On the other hand, the cascade process requires maintenance of low pH to minimize bacterial infection. It operates at a pH near 3.5, thus requiring stainless steel construction and consequently higher investment.

Prior to the advent of fully-computerized fermentor control, including automated cleaning-in-place (CIP) systems, labor costs favored cascade operation. With today's automation and simplified design, labor costs associated with operating either fermentation technology are negligible.

Distillation and dehydration

The first distillation step in the production of

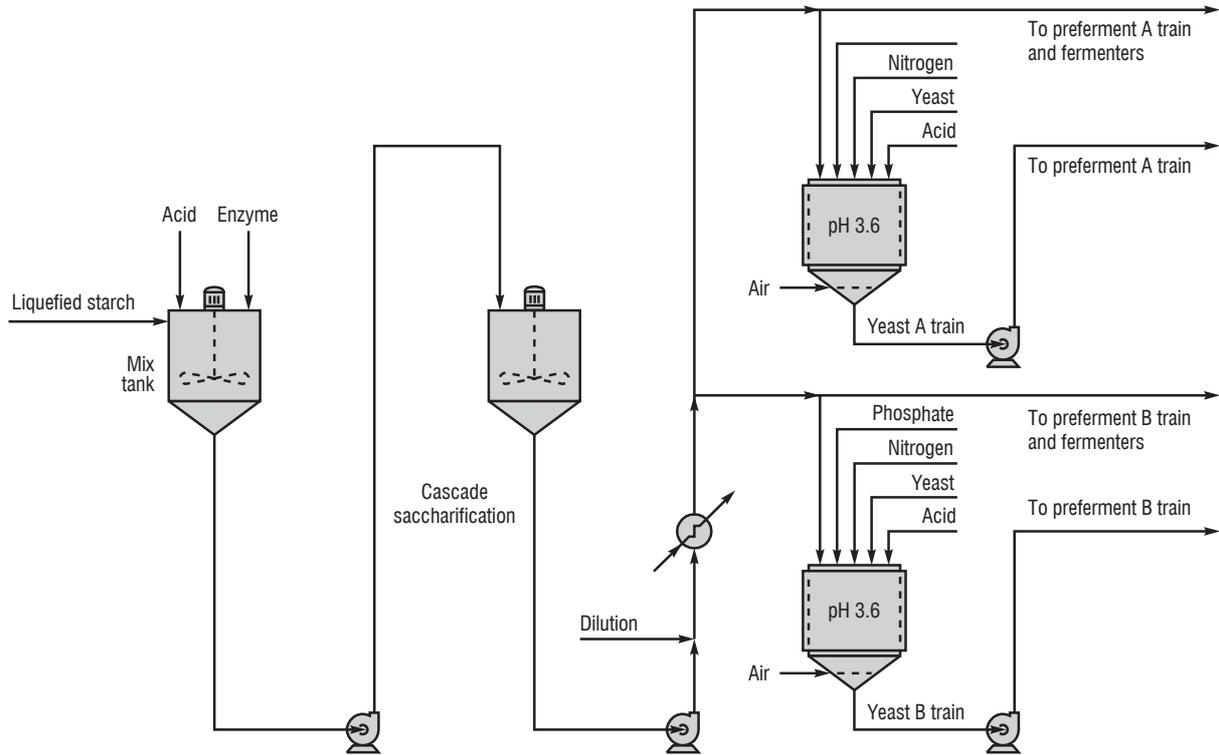


Figure 3. Cascade saccharification and yeast propagation.

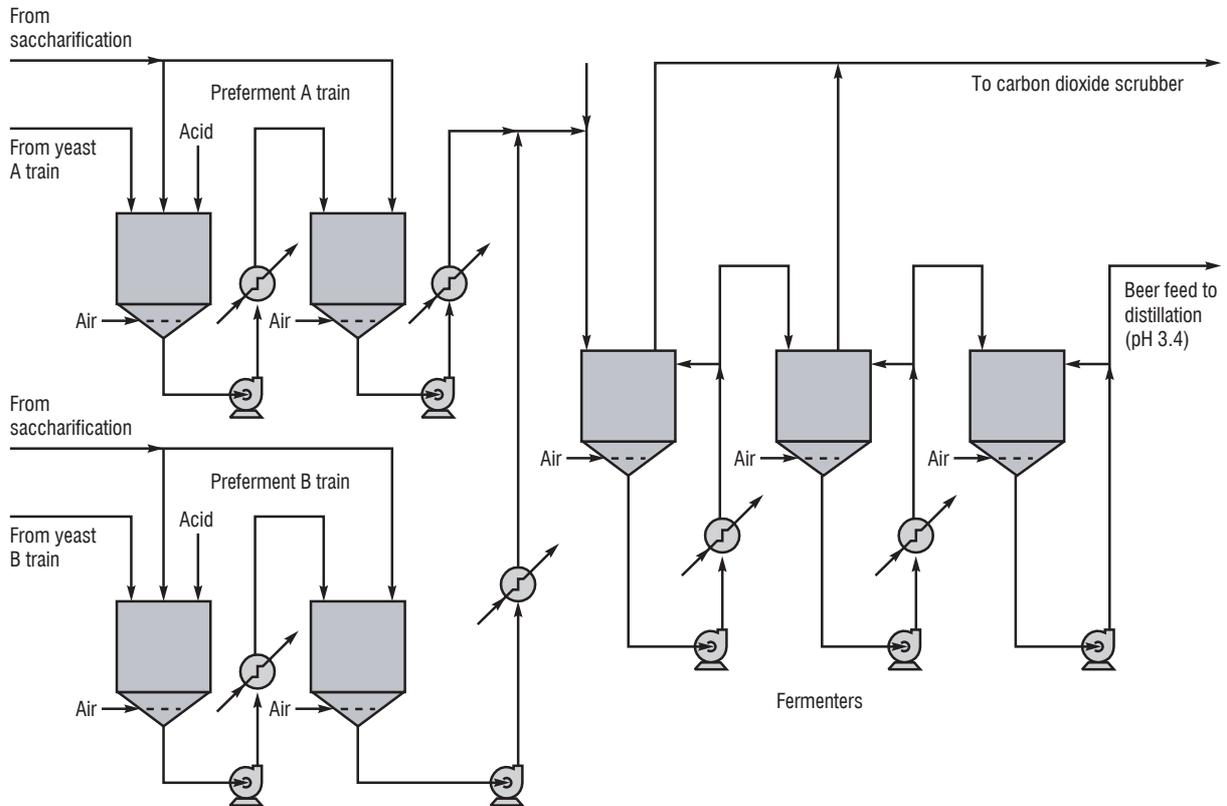


Figure 4. Cascade prefermentation and fermentation.

MFGE from fermented beers in the range of 8-12 wt % ethanol has been carried out primarily by techniques similar to those found in the beverage spirits industry. However, the dehydration step, primarily conducted by ternary azeotropic distillation in the past (Figure 5), has been superseded by molecular sieve dehydration utilizing integrated pressure swing adsorption (PSA) technology (Figure 6), particularly in newer installations.

Considerable research efforts have been expended in the field of ternary azeotropic dehydration, utilizing agents such as benzene, cyclohexane, diethyl ether and n-pentane, to reduce the assumed high energy consumption of this process. However, in reality many systems have been operating with multistage distillation such that the dehydration process is operated entirely with recovered heat from the primary distillation system. Alternatively, recovered energy from dehydration is used to provide most of the energy for stripping and rectification. Commercial systems are producing MFGE from fermented beer with thermal energy

consumption of 17,000 BTUs per gallon for combined distillation and dehydration. When molecular sieves are used in a well-integrated design, this operation consumes about 14,000 BTUs per gallon.

MOLECULAR SIEVE DEHYDRATION

Molecular sieve adsorption technology for dehydrating MFGE has been actively developed since the late 1970s. Pressure swing adsorption is now the technology of choice for MFGE dehydration for new plants and retrofits. Once believed to apply only to small production facilities, a single-train molecular sieve unit has been in operation in Brazil since 1993 with an annualized capacity of more than 60 million gallons.

Molecular sieves are hard, granular substances, spherical or cylindrical extrudates manufactured from materials such as potassium aluminosilicates. They are graded according to the nominal diameter of the myriad of internal pores that

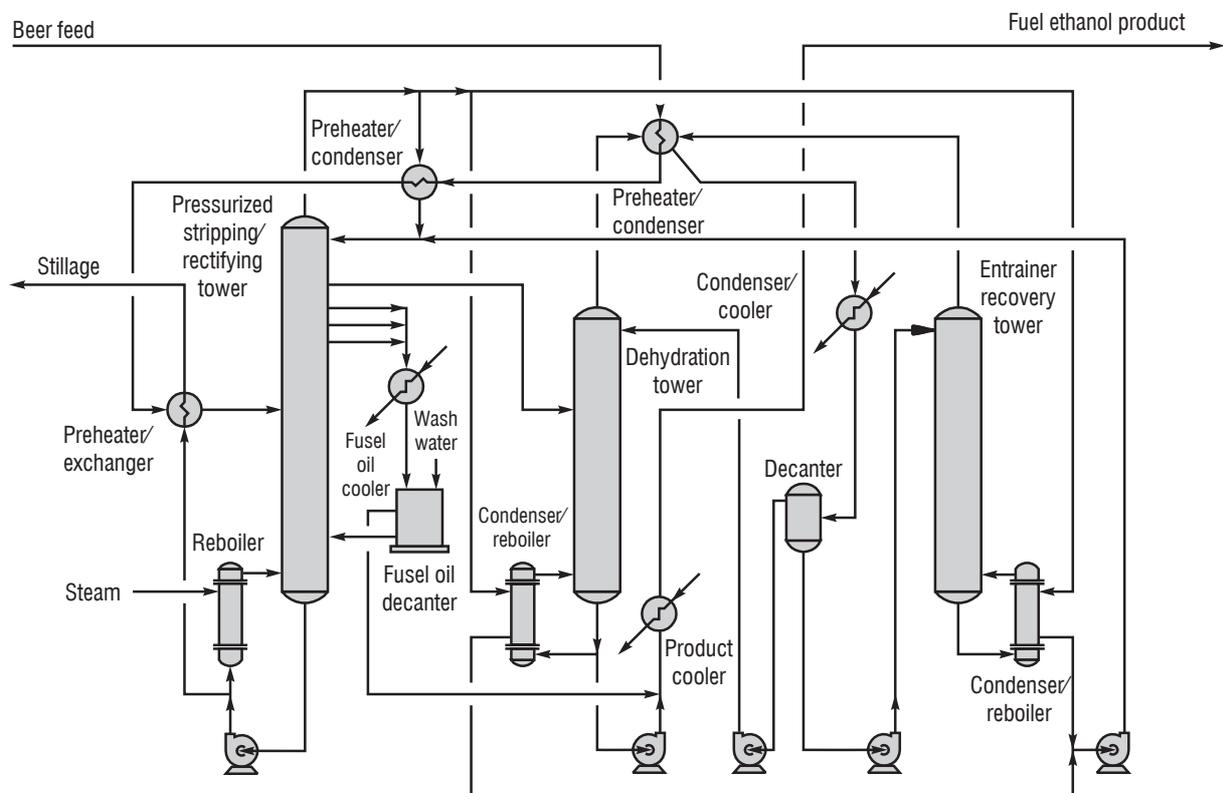


Figure 5. MFGE distillation and dehydration by ternary azeotrope.

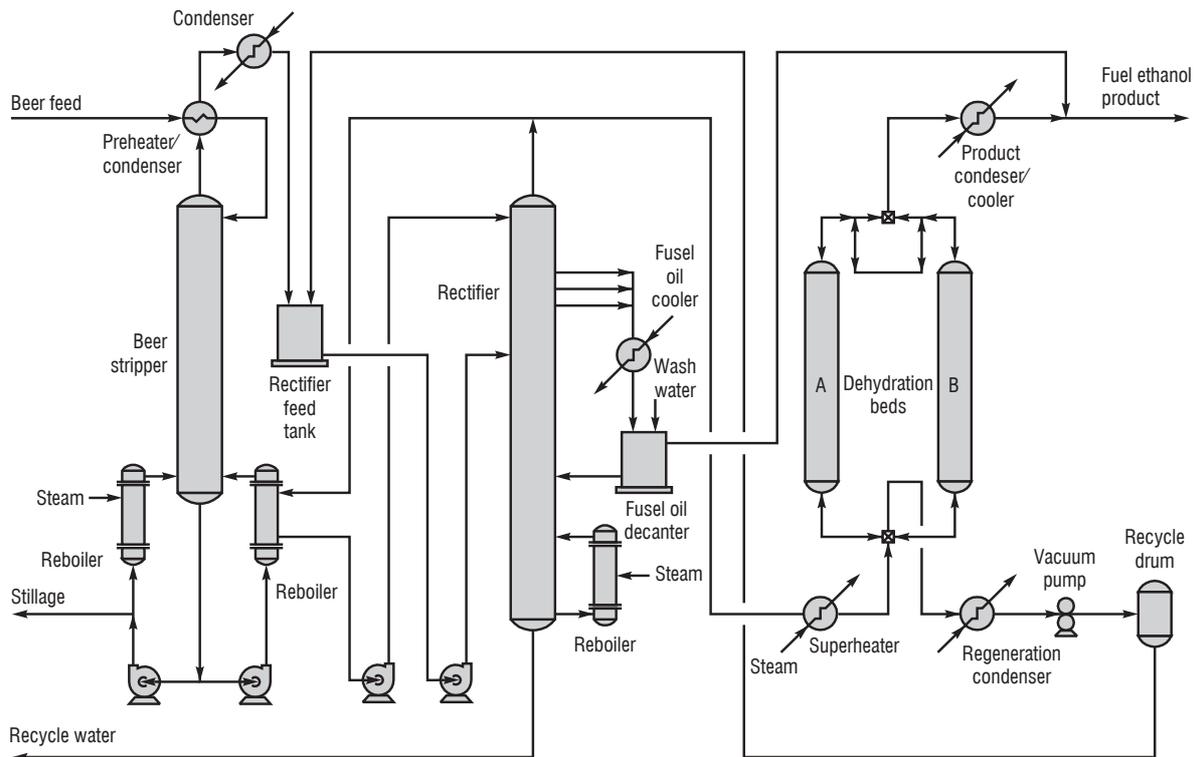


Figure 6. MFGE distillation and dehydration by pressure swing adsorption molecular sieve.

provide access to the interstitial free volume found in the microcrystalline structure. A typical grade used in ethanol dehydration is Type 3Å. This designation means that the average diameter of the interstitial passageways is 3 Angstroms (Å). (One Angstrom is a unit of measure equivalent to 10^{-8} centimeters). Thus, the passageways in the structure have a diameter that is of molecular scale. The water molecule has a mean diameter less than 3Å, while the ethanol molecule has a mean diameter greater than 3Å. In addition, the water molecules can be adsorbed onto the internal surface of the passageways in the molecular sieve structure. It is this combination of physical properties that make molecular sieves useful for the separation of mixtures of ethanol and water.

Water molecules can invade the inner structure of the molecular sieve beads and be adsorbed thereon, while the ethanol molecules are too large and pass out of the vessel leaving the water behind. Thus, dehydration of MFGE from sub-azeotropic concentrations is possible. It should be noted that this sieving process works to separate ethanol-water mixtures in either the

liquid or vapor phase. Process details of course differ for vapor and liquid mixtures.

The earlier systems for such dehydration, particularly in the liquid phase, required hot gas regeneration to displace the water from the beads. The molecular sieve beads rapidly deteriorated due to excessive thermal shock. With a half-life for the beads on the order of six months in the liquid systems, operating costs were high.

Application of vapor phase, pressure swing, vacuum purge adsorption (PSA) technology for MFGE dehydration matured in the 1980s. With PSA technology, molecular sieve beads are regenerated by recycling a portion of the superheated, anhydrous ethanol vapors to one bed under vacuum while the other bed is producing anhydrous ethanol vapor under pressure. With this milder regeneration condition, molecular sieve bead life is extended to several years. In some cases molecular sieve beads have operated for more than 10 years with no appreciable deterioration. This results in insignificant adsorbent replacement expense and reduced overall operating costs.

With an automated operation, the vapor feed to the molecular sieve system can be taken directly from a pressurized rectifier, with the reprocessing of the hydrous regeneration stream in the same rectifier. In this way, recovery of the ethanol from the molecular sieve regeneration system adds less than 1% to the distillation energy consumption.

One of the major shortcomings of the early molecular sieve systems was the high maintenance cost of the compressor used to pressurize feed vapor from atmospheric pressure rectifiers. This problem was initially solved by feeding a liquid spirit to a pressurized vaporizer, thereby eliminating the compressor. However, higher energy consumption resulted. These problems have been overcome by new pressure-cascaded distillation systems integrated with the molecular sieve beds as shown in Figure 6. The rectifier is maintained at a pressure sufficient to economically operate a reboiler to provide energy to the atmospheric pressure beer stripper. Approximately two-thirds of the overhead rectifier vapor is used to provide this reboiler energy. The remaining ethanol spirit vapor is passed through a steam-heated superheater and then to the molecular sieve beds for dehydration. The thermal energy content of the resultant superheated anhydrous ethanol vapor can be recovered in an auxiliary reboiler on the beer stripper. The condensed anhydrous ethanol vapors (MFGE) are then cooled and passed to storage. The recovered ethanol and water from the regeneration phase of the pressure swing adsorption cycle is recycled to an appropriate feed point in the rectifier for recovery.

Animal feed co-products

The DDGS co-product operation for dry milling plants recovers the residual non-starch materials in the stillage from the beer stripper. This is accomplished by combining centrifuged solids (wet cake) with concentrated solubles (syrup) from the evaporated thin stillage after centrifugal separation, as shown in Figures 7 and 8. Recycle of dried DDGS acts as a base for blending the wet cake and syrup to yield a material suitable for operation of dryers, which may be either hot-gas or steam-tube type. The DDGS product meets the commercial specification of 26-30%

crude protein. However, the more efficient dry milling plants produce DDGS containing 30-35% protein and 8-9% fat as well as B complex vitamins from yeast propagated in the fermentation operation. This is a high-value, triple concentrate of the corn protein and oil, plus the incremental value of the propagated yeast.

In the wet milling industry, the primary animal feed co-product is corn gluten meal (CGM), a high value, low volume product containing 60% protein, but no appreciable fat or oil. The secondary animal feed co-product is corn gluten feed (CGF), which is a concentrate of the residual fiber and liquid containing about 20% protein and very little fat or oil. This is a relatively low grade product compared to DDGS.

Energy use

Confusion abounds regarding energy use and efficiency of production of MFGE from corn. Some publications refer to very high steam usage, which is related to older practices in production of potable ethanol of various types from grain. Those operations hark back to an age when energy was cheap and potable ethanol had a high value. However, modern MFGE plants are designed with a high degree of efficiency with respect to energy consumption.

In wet milling operations, much of the energy use is charged to products other than ethanol. The ethanol operation itself requires only about 30,000 BTUs per gallon.

Dry milling operations charge all of the energy consumed to MFGE production, although much of this energy use is associated with production of the DDGS co-product. As an example of the efficiency of modern operations, thermal energy use of 35,000 BTUs of fuel and electrical use of 1.15 kilowatt hours per gallon is common. These usages can be compared with the gross heating value of ethanol, which is 84,000 BTUs per gallon, or the net heating value of about 75,000 BTUs per gallon.

Investment

Facilities for production of MFGE from corn vary widely in size and technology base; it is therefore

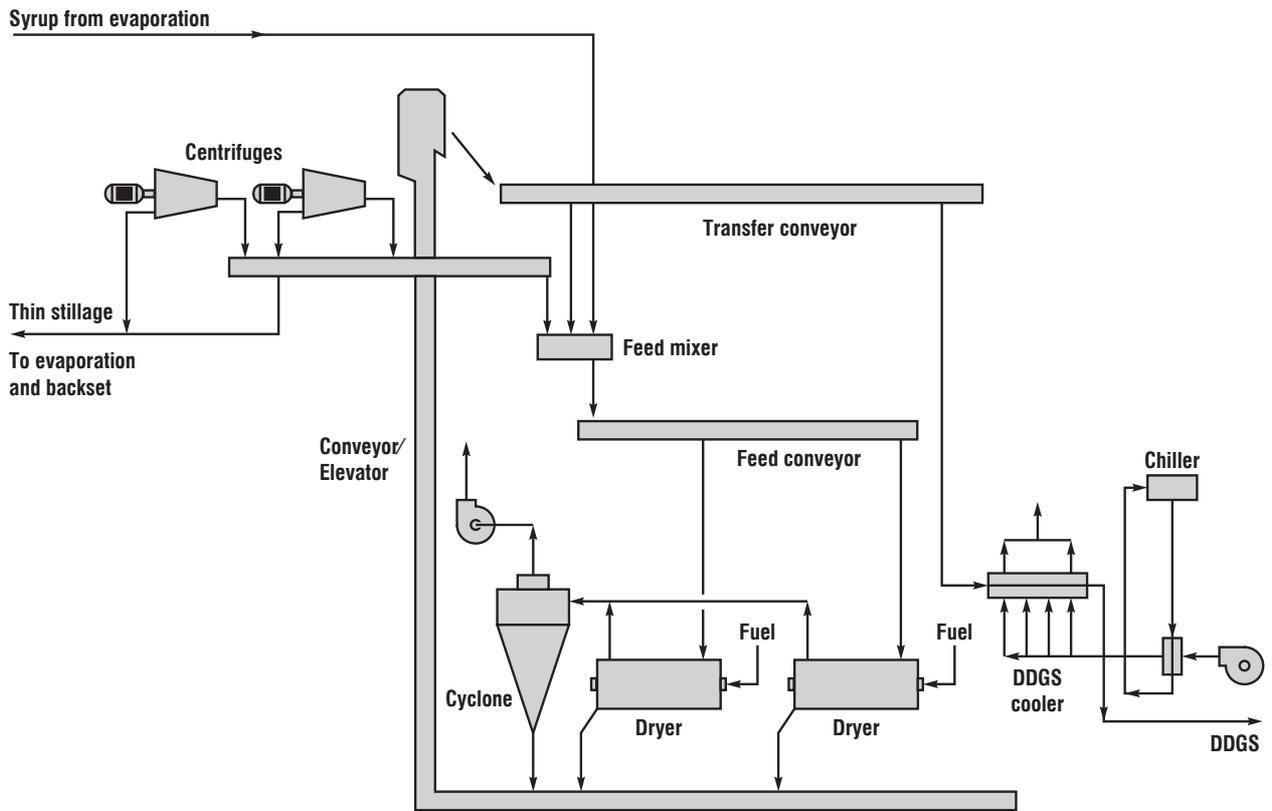


Figure 7. Centrifugation and drying.

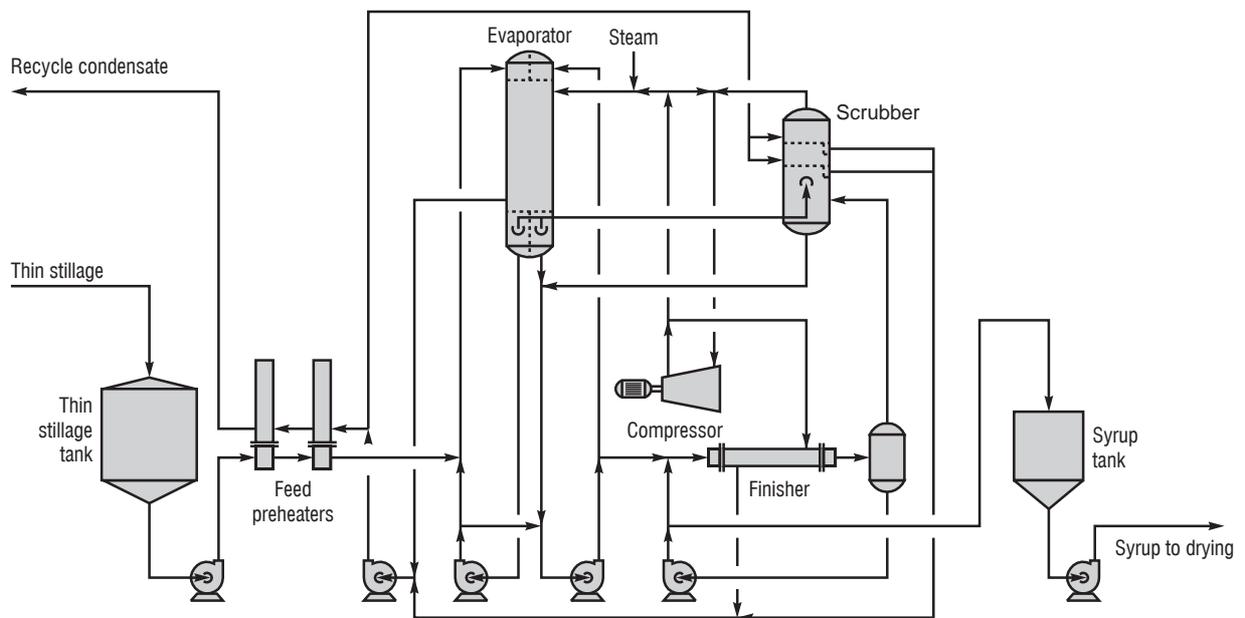


Figure 8. Evaporation.

difficult to set a standard investment factor. In addition to large scale wet milling and dry milling facilities, there are smaller plants built for unique opportunities, such as low cost waste feedstocks, or adjacent cattle feedlots that can utilize the stillage directly. In effect, investment for any particular facility must be developed on a site-specific basis for the conditions at hand.

Experience in developing improved and simpler technology over the previous decades permits estimation of approximate costs for wet milling and dry milling facilities in view of the most advanced and efficient technology available. Total investment relating to large dry milling plants (turnkey) approaches \$1.75 per gallon of annual capacity (denatured basis). It should be noted that in general, wet milling MFGE production units require only about half the investment of a dry milling plant. This is due to the fact that an MFGE facility is simply added on to a wet milling plant. All other facilities, such as raw material handling, primary processing, waste processing and utilities are already in place and provide sufficient capacity for the adjacent ethanol facility.

At the other extreme, small farm-based ethanol plants with direct acquisition of feed-stocks and access to cattle feedlots for direct consumption of wet stillage can be built to produce in the range of 5-30 million gallons per year for investments in the range of \$2.00 to \$1.50 per annual gallon. However, in special situations, using pre-owned equipment, the required investment may be less than \$1 per annual gallon of capacity.

References

- Bowman, L., and E. Geiger. 1984. Optimization of fermentation conditions for alcohol production. *Biotechnology and Bio-engineering* 26:1492.
- Hill, L.L. *et al.* 1986. South Point Ethanol 60-Million-Gallon-per-Year Fuel-Ethanol Plant Final Technical Report. Prepared for: US Department of Energy, DOE/ID/12188.
- Katzen, R. 1987. Large-scale ethanol production update. *Alcohol Fuels* 1987, Cancun, Mexico.
- Katzen, R. and P.W. Madson. 1991. Bio-engineering improvements in corn fermentation to ethanol. *Corn-Derived Ethanol Conference*, Peoria, Illinois, May 12-21.
- Katzen, R., P.W. Madson and B.S. Shroff. 1992. Ethanol from corn. State-of-the-art technology and economics. *AICHe Annual Meeting, Biotechnology for Fuels, Chemicals, and Materials*, Session No. 154, Miami Beach, Florida, November 1-6.
- Kemmerling, M.K. 1989. Effects of bacterial contamination on ethanol yield and downstream processing. *International Conference on Alcohols and Chemicals from Biomass*, Guadalajara, Mexico.
- Madson, P.W. 1990. Bio-ethanol experiences in the USA. *Zuckerind* 115 No. 12, pp.1045-1048.
- Madson, P.W. and J.E. Murtagh. 1991. Fuel ethanol in USA: review of reasons for 75% failure rate of plants built. *International Symposium on Alcohol Fuels*, Firenze '91, Florence, Italy.
- Raphael Katzen Associates. 1978. Grain Motor Fuel Alcohol Technical and Economic Assessment Study. Prepared for: US Department of Energy, HCP/J6639-01.

