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Recovery of Volatile Products from Dilute High-Fouling Process Streams

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Abstract

As biomass hydrolysis and fermentation technologies approach commercial viability, advancements in product recovery technologies will be required. For cases in which fermentation products are more volatile than water, recovery by distillation is often the technology of choice. Distillation technologies that will allow the economic recovery of dilute volatile products from streams containing a variety of impurities have been developed and commercially demonstrated. Distillation tower and tray designs, along with specialized heat-exchanger designs, allowing for extended processing intervals on solutions containing lignocellulosic residues, organic acids, and inorganic salts concentrations >100 g/L are in commercial operation. In the case of ethanol, distillation energy consumption efficiencies for processing solutions containing <40 g/L of desired product can approach demonstrated energy consumption efficiencies for solutions containing concentrations >120 g/L. These proprietary technologies have been applied individually at commercial scale, and designs have been developed that incorporate the combined technologies with only a marginal increase in capital investment compared to traditional methods.

Index Entries: Distillation; energy consumption; fouling; product recovery; separation.

Introduction

Since the 1960s, significant developments have occurred in the field of biotechnology to produce fuels and chemicals from low-cost feedstocks such as biomass. Processing challenges have been and continue to be encountered with advancements in the conversion of the cellulose and hemicellulose fractions of biomass to fermentable sugars and subsequently to fuels and chemicals. Most cellulose and hemicellulose hydrolysis technologies result in process streams high in residual solids that include unconverted polysaccharides, ash, and lignin-based compounds. In addition,

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many acid hydrolysis technologies produce "beers" saturated with calcium salts. Advances in hydrolysis and fermentation technologies have allowed the production of fuels and chemicals from substrates previously considered impractical sources. However, in most of these cases, product concentrations are low, and the crude product-containing broth also contains substantial fouling material.

Inherent in distillation systems for these complex feedstocks is the challenge of mechanical design to achieve the process separation objectives, while simultaneously allowing for commercially practical cleaning cycles. The traditional complex tray designs, such as bubble caps, valve trays, and other proprietary tray designs, perform well as mass-transfer devices for the volatile materials separations desired. Unfortunately, these complex tray designs are sensitive to the presence of fouling materials that, although not participating in the mass-transfer equilibria, diminish the functionality of the trays by virtue of buildup in the active mass-transfer zones. This accumulation of fouling results in diminished system performance in the form of reduced hydraulic throughput (production rate) or reduced efficiency of volatiles separation. In either case, commercial results suffer. In this article, we present a novel distillation tray design that has been demonstrated to be effective when confronted with the challenge of fouling feedstocks typically found in biomass conversion systems.

Bioconversion technologies also frequently produce solutions containing the desirable bioproduct in concentrations of <100 g/L, and in many cases <40 g/L. Traditional designs for distilling such dilute mixtures require excessive energy to achieve the desired separations. We address this problem by reporting on commercial experience with dilute feedstocks when distilled with novel energy-integration designs and thermal-cascading systems. Furthermore, we report on the expected performance of proprietary integrated designs that substantially improve the energy consumption efficiency when distilling dilute feedstocks.

Distillation Tray Design

Distillation internals (trays) (Fig. 1) perform four distinct functions:

1. Mix rising vapor with falling fluid
2. Provide for separation after mixing
3. Provide a path for liquid to proceed down the tower
4. Provide a path for vapor to proceed up the tower

Distillation is typically a countercurrent vapor/liquid mass-transfer system. Liquid descends by gravity through directed channels (downcomers) and is repeatedly distributed over plate areas that contain a large number of vapor channels. The vapor channels provide high-velocity jets of vapor that pass upward to mix intimately with the liquid flowing across the plate area. This mixing of vapor and liquid results in a close approach to equilibrium among the volatile components. The mixture of vapor and

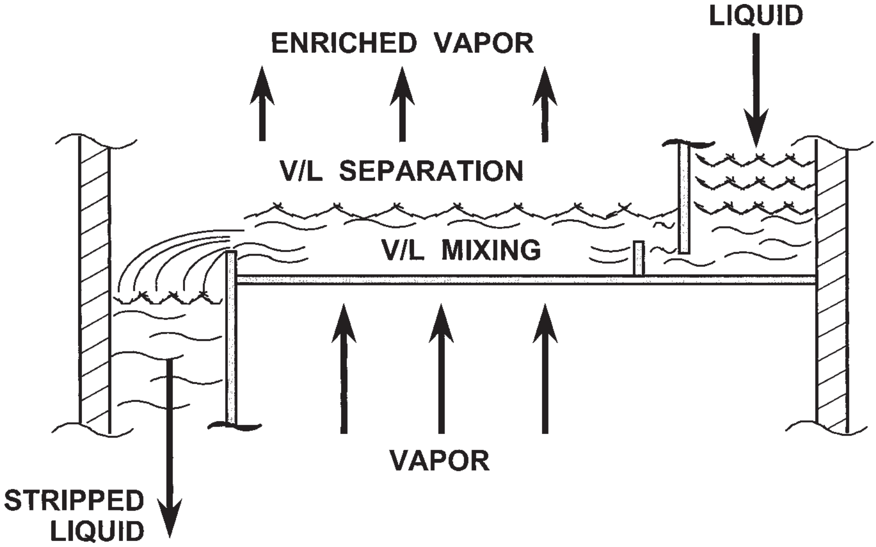

Fig. 1. Distillation tray functions. V/L, vapor/liquid.

liquid is then allowed to separate in a low-velocity zone, with the enriched vapor (essentially free from substantial entrained liquid) passing upward to the next tray. The stripped liquid passes downward through its separate downcomer to the tray below for repeat of the functions. The downcomer is designed to promote disengagement of vapor bubbles so that the descending liquid will be essentially free of entrapped vapor. Perforated ("sieve") trays are exemplary of the conventional distillation tray design (Fig. 2).

Although conventional distillation tray designs have been used satisfactorily for decades in processing a variety of fouling feedstocks, the more complex and concentrated the fouling feedstock becomes, the more commercially unsatisfactory conventional distillation trays become. Figure 3 shows a typical fouling profile that develops on conventional trays. The most common fouling is a matrix of inorganic salts, resins, gums, protein, and fiber that collects on metal surfaces by crystallization, adhesion, and physical entrapment. Fouling is initiated at the vapor/liquid interface owing to thermal and concentration gradients. Conventional trays (e.g., perforated) initiate mass and energy transfer at the metal surface, thereby promoting the initiation of fouling at the edge of the vapor passages. This fouling builds up within the vapor passages as the system continues to operate.

Functionality of the tray can become seriously impaired with even modest amounts of fouling. For trays operating at peak capacity and efficiency, a 10% loss of the vapor passage diameter (e.g., a fouling buildup of 0.5 mm around the periphery of a 10 mm-diameter vapor passage) results in a 19% loss of capacity. As fouling progresses, the vapor velocity through the constricting passages increases to the point that fouling material is

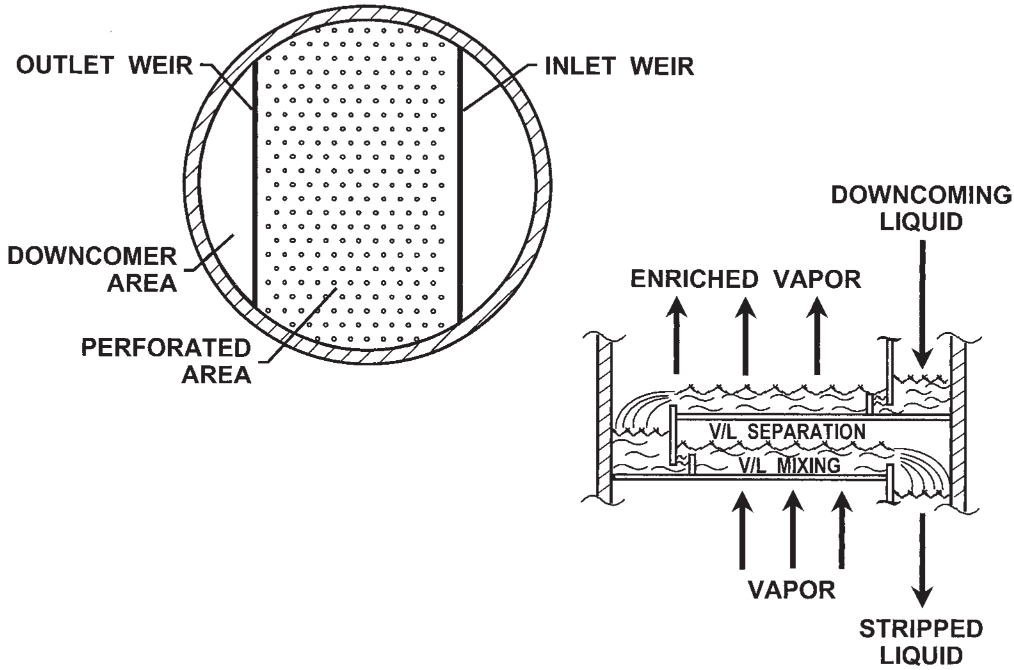

Fig. 2. Perforated trays in countercurrent cascade. V/L, vapor/liquid.

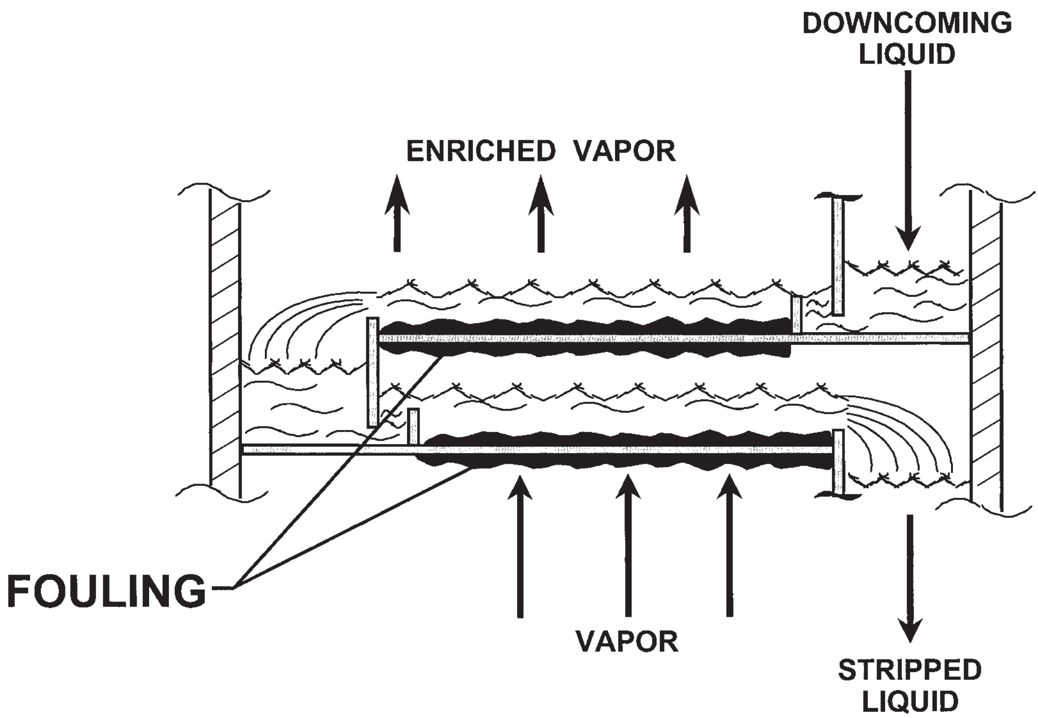

Fig. 3. Typical fouling profile of perforated distillation trays.

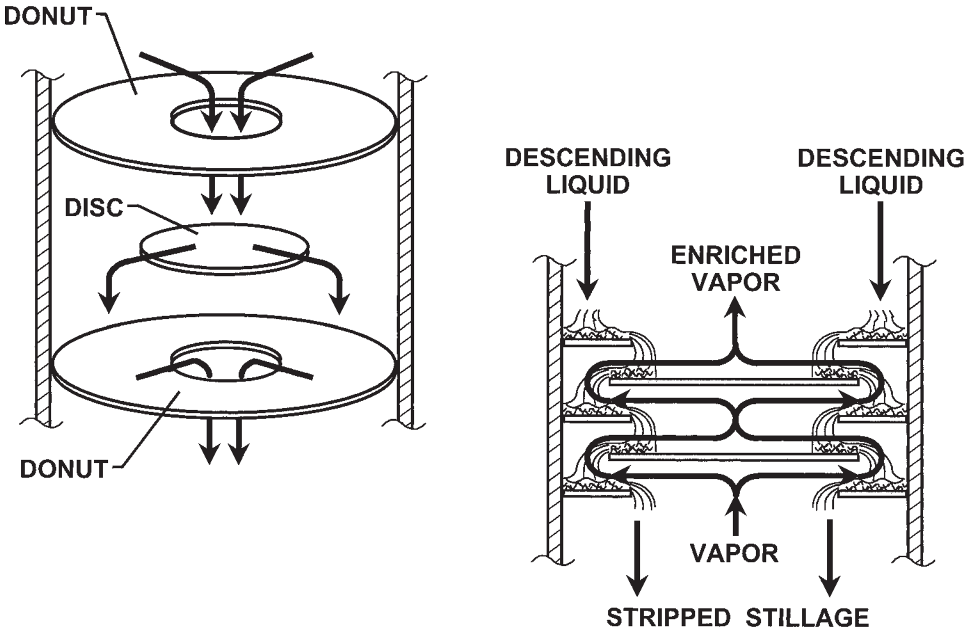

Fig. 4. Disc/donut trays.

carried upward with the vapor jet, impinging on the bottom of the tray above, resulting in further fouling. There are several commercial examples in which it is necessary to shut down and clean the distillation trays as frequently as once per week.

During the 1960s, substantial activity was initiated in the pulping industry to improve the economics of recovery (by distillation) of value-added products from spent pulping liquor. Because of the extraordinary fouling potential of these liquors, an effort was undertaken to develop an alternative system that could perform the desired mass-transfer functions, while simultaneously exhibiting a high degree of tolerance to fouling. This effort led to the development of disc/donut trays (Fig. 4) *(1)*.

The key to understanding the fouling tolerance of disc/donut trays is in the observation that the mass transfer occurs in the open space between metal surfaces (the liquid "curtain"). Furthermore, it is observed that the areas of buildup of the fouling material are separate from the mass-transfer zone; that is, the fouling material tends to collect in the nonfunctional, quiescent zones of the trays (Fig. 5). This is distinctly different from the conventional tray in which mass transfer is initiated by vapor/liquid contact as the vapor bubble emerges from the hole in the tray. It is at this vapor/liquid/tray interface that thermal and concentration gradients initiate the precipitation and crystallization of the fouling compounds. The crystallized fouling compounds contaminate the metal surface and accelerate further fouling. The accumulation of fouling components interferes with the functioning of the mass-transfer zone by changing the shape and size of the vapor passages.

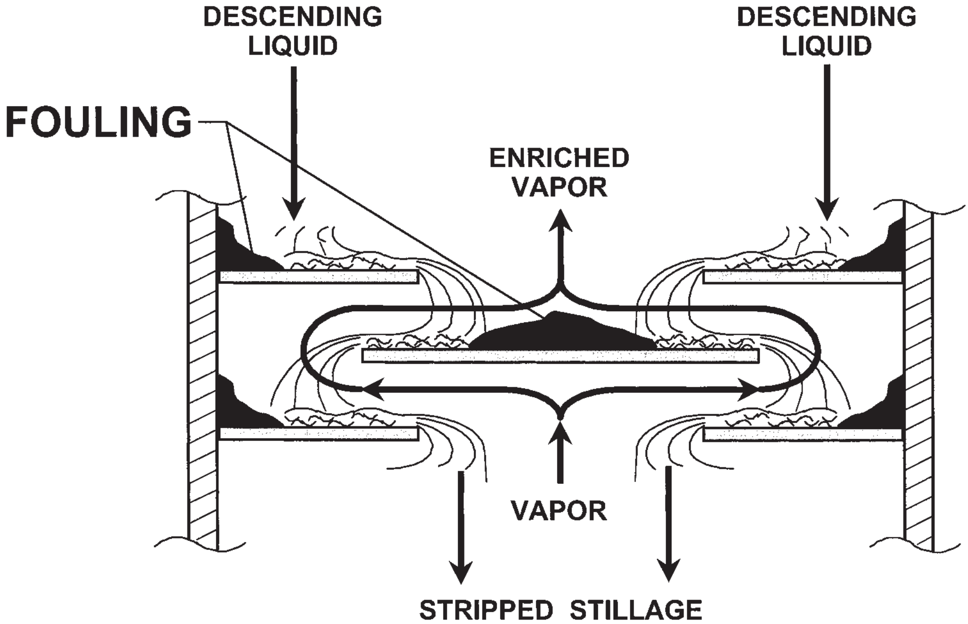

Fig. 5. Typical fouling profile of disc/donut trays.

The disc/donut system, on the other hand, develops a curtain of liquid descending through free space between each donut and disc, and between each disc and donut. The vapor and liquid contact, therefore, takes place remote from the tray surface, causing the fouling culprits to agglomerate and deposit in the quiescent areas at the center of the discs and against the tower wall at the periphery of the donuts. Because these areas do not participate in the mass-transfer operation, large buildups of fouling material can occur and yet have no impact on the functionality of the mass-transfer zone.

This disc/donut technology has been successfully applied in a variety of commercial installations processing feedstocks such as sulfite-pulping liquor, fermented sulfite-pulping liquor, fermented lignocellulose hydrolysate, fermented whole-grain mash, ALCELL® pulping liquor, fermented blackstrap molasses, and fermented cheese whey (Table 1; *see* pages 1056 and 1057). In most cases, the fouling material continually sloughs off at a rate in equilibrium with its development. This has led to extraordinarily long cycles between cleanings. In one case, the cycle was extended from 1 wk with conventional trays to 1 yr with the converted disc/donut system (McCarthy, M., personal communication). In another case, processing fermented whole-grain dry-milled beer, the cleaning cycle was extended to 5 yr (Conway, D., personal communication). Another measure of the applicability of the disc/donut system is that, for most cases, antifoam and antiscalant chemicals can be eliminated from the process.

The critical design parameters for disc/donut systems are the vapor-loading factors *(2)*. The "curtain factor" specifies the vapor loading in the

$$\text{"curtain factor"}, \quad f_h = U_h\left(\frac{\rho_v}{\rho_l - \rho_v}\right)^{1/2} = 0.06\text{–}0.24 \text{ m/s}$$

$$\text{"separation factor"}, \quad f_v = U_v\left(\frac{\rho_v}{\rho_l - \rho_v}\right)^{1/2} = 0.03\text{–}0.12 \text{ m/s}$$

f = loading factor (m/s)

U_h = horizontal vapor velocity (m/s) evaluated through the cylindrical liquid curtain

U_v = vertical vapor velocity (m/s) evaluated in the cylindrical space between disc pairs and in the annular space between donut pairs

ρ_l = liquid density (g/cm^3)

ρ_v = gas density (g/cm^3)

Fig. 6. Design loading factors for disc/donut trays.

free-fall space traversed by the curtain of liquid as it descends from the periphery of the donut hole to the disc, and as it descends from the periphery of the disc to the donut (Fig. 6). The curtain factor determines the effectiveness of the mass-transfer zone. As the curtain factor increases, mass-transfer efficiency improves until a sharp discontinuity occurs above 0.24 m/s, at which point the curtain zone floods. Conversely, as the curtain factor decreases below about 0.06 m/s, vapor/liquid mixing becomes unstable and mass-transfer efficiency drops rapidly.

In a similar but converse manner, the "separation factor" determines the effectiveness of the liquid/vapor separation (disengagement) zones in the vertical cylindrical area above each disc and in the vertical annular area above each donut. As the separation factor increases, the liquid/vapor separation efficiency decreases. Above about 0.12 m/s, disengagement efficiency falls to unacceptable levels for commercial operation, and the system becomes hydraulically unstable, resulting in flooding of the separation zones. For practical economic considerations of the equipment, a lower limit for design of the separation factor is established at 0.03 m/s. However, note that separation efficiency continues to improve, but at a marginal rate, below 0.03 m/s.

It can be determined from the relationships defined by the design loading factors that, for a given energy input at a given operating pressure, certain geometric relationships must exist and that a given design represents a compromise between mass-transfer efficiency and separation efficiency. Because the loading factors are dependent on gas velocity, for any given vapor/liquid system, the mechanical design considerations for tower

Table 1
Installations of Disc/Donut Distillation

Company	Location	Year	Application	Fouling considerations
Commercial Alcohols	Temiscaming, Quebec, Canada	1965	Stripper for fermented calcium-based sulfite-pulping liquor	Foam, fiber, scale
ITT Rayonier	Grays Harbor, WA	1967	CO_2 stripper and SO_2 stripper following soda ash neutralization of sodium-based sulfite-pulping liquor	Foam, fiber, scale
Georgia-Pacific	Bellingham, WA	1971	SO_2 stripper	Pressurized, foam, fiber, scale
Rayonier Quebec	Port Cartier, Quebec, Canada	1971	SO_2 stripper, ammonia-based sulfite-pulping liquor	Pressurized, foam, fiber, scale
ITT Rayonier	Fernandina, FL	1974	SO_2 stripper, ammonia-based sulfite-pulping liquor	Pressurized, foam, fiber, scale
Gulf Oil Chemicals	Pittsburgh, KS	1977	Stripper for fermented cellulose	Fiber, sludge, filamentous fungus
South Point Ethanol	South Point, OH (purchased by ADM in 1997)	1980	Stripper for fermented corn (dry mill)	Foam, fiber, scale, protein pressurized (300°F): 8-mo cleaning cycle
Reeve Agri-Energy	Garden City, KS	1981	Stripper for fermented corn/milo (dry mill)	Foam, fiber, scale, protein pressurized (300°F): cleaning by caustic on-the-run
Biological Energy	Valley Forge, PA	1982	Stripper for organocel-pulping liquor	Lignin, resins, gums, fiber
Shepherd Oil	Jennings, LA (currently operating in Aurora, NE)	1984	Stripper for fermented molasses/corn/milo (dry mill)	Foam, fiber, scale pressurized (270°F)

ALCELL Developments	Newcastle, New Brunswick, Canada	1989	Ethanol/water stripper for ALCELL® pulping liquor	Lignin, resins, gums, fiber
Reeve Agri-Energy	Garden City, KS	1992	Stripper for fermented corn/milo (dry mill)	Foam, fiber, scale, protein: 5-yr cleaning cycle
Manildra Group	Nowra, NSW, Australia	1996	Stripper for fermented wheat starch	Foam, scale, protein
Minnesota Energy	Buffalo Lake, MN	1996	Stripper for fermented corn (dry mill)	Foam, fiber, scale, protein: 2-yr+ cleaning cycle
Bacardi	San Juan, Puerto Rico	1997	Stripper for fermented unclarified blackstrap molasses	Foam, scale, protein: 1-yr cleaning cycle
Georgia-Pacific West	Bellingham, WA	1997	Ammonia stripper for spent pulping liquor	Foam, fiber, scale, lignin
Carbery Milk Products	Ballineen, County Cork, Ireland	1998	Stripper for fermented cheese whey	Foam, scale, protein
API Grain Processors	Red Deer, Alberta, Canada	1998	Stripper for fermented wheat starch (A and B)	Foam, scale, protein
Sunrise Energy	Blairstown, IA	1999	Stripper for fermented corn (dry mill)	Foam, fiber, scale, protein

Table 2
Installations of Fouling-Tolerant Heat-Exchange Systems

Company	Location	Year	Application	Fouling considerations
South Point Ethanol	South Point, OH	1980	Fermented corn (dry mill)	Fiber, scale, protein pressurized (300°F)
Reeve Agri-Energy	Garden City, KS	1981	Fermented corn/milo (dry mill)	Fiber, scale, protein pressurized (300°F)
Shepherd Oil	Jennings, LA (currently operating in Aurora, NE)	1984	Fermented molasses/corn/milo (dry mill)	Fiber, scale pressurized (270°F)
ALCELL® Developments	Newcastle, New Brunswick, Canada	1989	ALCELL® pulping liquor	Lignin, resins, gums, fiber
Reeve Agri-Energy	Garden City, KS	1992	Fermented corn/milo (dry mill)	Fiber, scale, protein
Manildra Group	Nowra, NSW, Australia	1996	Fermented wheat starch	Scale, protein
Minnesota Energy	Buffalo Lake, MN	1996	Fermented corn (dry mill)	Fiber, scale, protein
API Grain Processors	Red Deer, Alberta, Canada	1998	Fermented wheat starch (A and B)	Scale, protein
Sunrise Energy	Blairstown, IA	1999	Fermented corn (dry mill)	Fiber, scale, protein

diameter, disc and donut-hole diameters, and disc-to-donut spacing are straightforward. For example, at constant disc-to-donut spacing and at constant tower diameter, increasing the disc and the donut-hole diameters decreases the curtain factor and the disc-to-disc separation factor, but increases the donut-to-donut separation factor. Also, at constant tower, disc, and donut-hole diameters, an increase in disc-to-donut spacing reduces the curtain factor but has no effect on the separation factor.

To support fouling-tolerant distillation towers, it is necessary to provide fouling-tolerant heat exchangers and alternative heat-transfer systems for such services as feed heating, bottoms cooling, and reboiling. These designs are proprietary, and the technical details are beyond the scope of this article. Table 2 lists projects in which fouling-tolerant heat-exchange systems have been commercially employed.

Distillation Energy Consumption

Because ethanol, in particular fuel ethanol, is the largest-volume biotechnology commodity, the need to develop the technology for improved, more energy-efficient systems has received substantial attention. The following discussion is based on energy-efficiency developments as they relate to distillation in the ethanol industry.

The traditional distillation system consists of a combined stripper and rectifier accepting fermentation broth as feedstock and separating it into two major components. The desired product is the near-azeotrope of ethanol with approx 5% (v/v) water. The second product ("stillage") contains the balance of water, inerts, fouling components, and only traces of ethanol. This combined stripper/rectifier technology exhibits an energy requirement vs feedstock concentration according to curve (A) in Fig. 7. During the era in which this technology dominated, typical fermentation feedstocks developed ethanol concentrations between 7 and 9% (v/v). Energy consumption per liter of ethanol was typically in the 5 to 6 MJ range. Advanced fermentation technologies developed in the grain-to-ethanol industry have raised commercial operations to the 12 to 13% (v/v) ethanol concentration range in the fermentation broth, lowering the required energy consumption to about 4.3 MJ/L of ethanol.

During the past 15 yr, advanced sugar- and starch-based ethanol plants have employed thermally integrated distillation technology in which the stripping and rectifying functions are separated, thermally integrated, and cascaded. The typical energy requirement is shown as curve (B) in Fig. 7. This technology, when employed to process the advanced fermentation broths, has reduced the energy requirement for the separation to about 3 MJ/L of ethanol.

Neither of these technologies is particularly suitable for the processing of low-concentration fermentation broth feedstocks (<7% [v/v]) because of the accelerating energy requirement as the concentration is reduced.

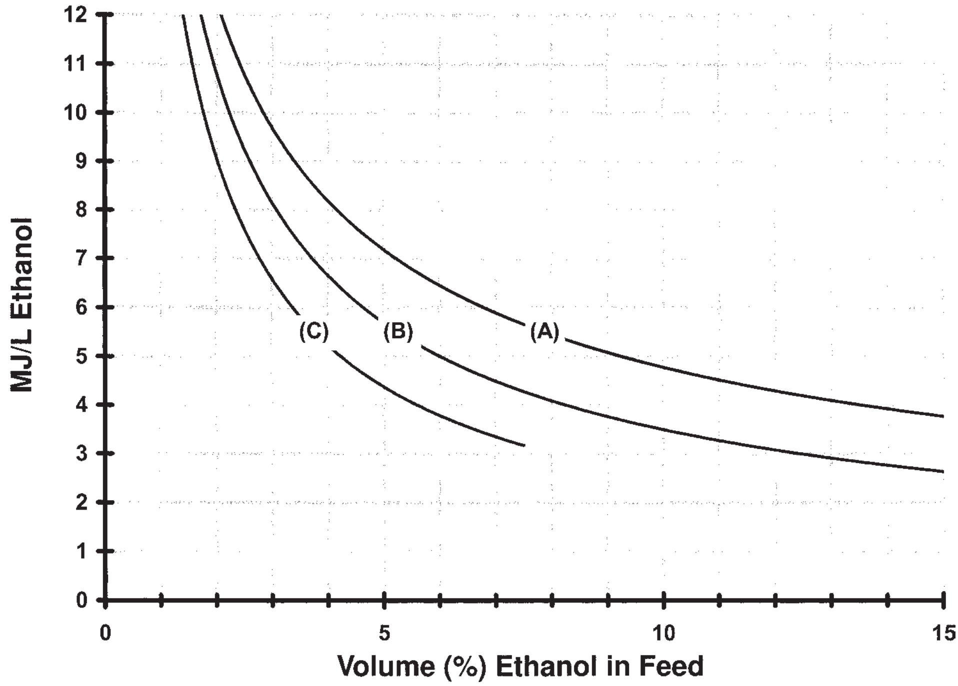

Fig. 7. Energy comparison for various distillation technologies: (A), traditional stripper/rectifier system; (B), thermally integrated stripper/rectifier system; (C), low-proof feed, thermally integrated stripper/rectifier system. Comparison is based on 95% (v/v) product, 0.02% (w/w) ethanol in bottom streams, and saturated feed.

During the late 1970s and early 1980s, a new approach to processing dilute feedstocks was demanded by the sulfite-pulping industry for ethanol recovery from waste-liquor fermentation. It was not uncommon for the fermentation broth to contain <3% (v/v) ethanol. The challenge was addressed in a different manner from that of the grain fermentation industry, because the expectation of substantial improvements in fermentation product concentration did not exist with sulfite liquor. To address this need, a technology was developed involving split strippers and rectifiers, thermally cascaded in an optimized fashion to minimize energy consumption *(3)*.

To address the commercial needs of the emerging ethanol-from-biomass industry, new approaches were required. By combining the applicable characteristics of thermally integrated stripper/rectifier technology with knowledge gained from the sulfite-liquor ethanol fermentation industry, new combined systems of thermally integrated and split distillation systems with cascaded energy recovery have been developed. The typical energy consumption characteristic (curve [C] in Fig. 7) shows that these systems' energy consumption, at 4% (v/v) feedstock, equals the traditional system's energy consumption at 9% (v/v). Furthermore, these new systems demand energy at 7% (v/v) feedstock which is equivalent to the systems recently employed in the United States with fermented feedstocks of 11% (v/v).

The energy consumption characteristics we have just described define the energy flow required into the battery limits of the distillation system. This energy can be provided either by direct boiler steam or by recovered energy from other plant operations. For example, many lignocellulose pretreatment processes exhaust low-level flash vapors that can be used to supply energy to distillation (e.g., reboilers). In addition, low- and midlevel energy that is rejected by the distillation system can be used across the battery limits for various process heating needs, such as boiler feedwater and process water for general use. In a total plant design, these types of energy integrations can play an important role in the cost of ethanol production.

Distillation system designs that yield further reductions in energy consumption for the processing of low-concentration mixtures have been developed. For commercial purposes, however, the more complex designs must be approached cautiously because of the rapidly accelerating ratio of investment-to-energy savings.

Conclusion

It is generally recognized that the first generations of commercially successful biomass conversion facilities will be faced with the challenge of dilute, high-fouling process streams from which a volatile product must be recovered. Traditional distillation systems do not provide the fouling tolerance nor the energy efficiency appropriate for a commercially competitive operation. By combining technologies from the chemical, petrochemical, pulping, and ethanol industries, distillation systems and equipment designs have been developed that can effectively process these biomass-based streams.

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