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Ethanol Production in a Membrane Bioreactor

Pilot-Scale Trials in a Corn Wet Mill

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Abstract

Pilot plant trials were conducted in a corn wet mill with a 7000-L membrane recycle bioreactor (MRB) that integrated ceramic microfiltration membranes in a semi–closed loop configuration with a stirred-tank reactor. Residence times of 7.5–10 h with ethanol outputs of 10–11.5% (v/v) were obtained when the cell concentration was 60–100 g/L dry wt of yeast, equivalent to about 10^9–10^{10} cells/mL. The performance of the membrane was dependent on the startup mode and pressure management techniques. A steady flux of 70 L/(m^2·h) could be maintained for several days before cleaning was necessary. The benefits of the MRB include better productivity; a clear product stream containing no particulates or yeast cells, which should improve subsequent stripping and distillation operations; and substantially reduced stillage handling. The capital cost of the MRB is \$21–\$34/(m^3·yr) (\$0.08–\$0.13/[gal·yr]) of ethanol capacity. Operating cost, including depreciation, energy, membrane replacement, maintenance, labor, and cleaning, is \$4.5–9/m^3 (\$0.017–\$0.034/gal) of ethanol.

Index Entries: Ethanol; membrane; corn wet mill; yeast.

Introduction

Environmental concerns about reducing automobile-polluting emissions, the clean air legislation in the United States, and the impending ban on methyl-tertiary butyl ether as an oxygenate have improved the potential market for ethanol production as a gasoline additive. Little has been done to improve the productivity of the traditional batch process for producing ethanol. Large increases in productivity have been recorded for continuous culture fermentations (50–300%) and immobilized whole-cell bioreactors

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(10–20 times higher productivity) *(1–4)*. However, these techniques present some drawbacks: washout for the continuous culture approach and gas holdup and high-pressure drops for immobilized cells.

A promising alternative is the membrane recycle bioreactor (MRB), which couples a continuous stirred-tank bioreactor to membrane modules to operate as a cell-recycle system. The main advantage of the MRB is that higher dilution rates can be achieved without washout because the cells are retained by the membrane and recycled back to the fermentor *(1–8)*. In addition, cell concentrations are typically 100–150 g/L on a cell dry wt basis, which is equivalent to cell counts of 10^9–10^{11}/mL. This is much higher than batch fermentations, which typically start with 15–25 g/L of yeast. The combination of these factors results in ethanol productivities that may be 5–20 times higher than for batch fermentors at ethanol concentrations of 75–100 g/L *(1–8)*. The MRB concept has been demonstrated successfully mostly on small laboratory-scale systems of 0.25–5 L *(3–8)*.

Recent advances in membrane technology and a decrease in membrane costs owing to increased competition has improved the prospects for the MRB. We had earlier demonstrated a 1500-L MRB for starch hydrolysis on-site at an ethanol plant *(9)*. In this article, we describe trials with a 7000-L MRB utilizing ceramic microfiltration membranes for ethanol production by fermentation. This was tested on-site at one of the largest corn wet-milling ethanol plants in the world. To bring it to this stage, the project went through three phases in three locations:

1. At our laboratories at the University of Illinois, where research into this concept was conducted to understand the kinetics and microbiology of the fermentation. Several membrane systems were screened and evaluated, the MRB was scaled up from 0.5 to 10 L, and the design of the 7000-L MRB was finalized and industrial partners were selected.
2. At Hudson, WI, where the MRB was fabricated by the engineering contractor (Niro Filtration) based on Phase 1 design and specifications.
3. At Pekin Energy (now Williams Energy), Pekin, IL. The MRB was installed and evaluated side-by-side with the present fermentation process. Further optimization of the MRB continued during this phase.

Because of space restrictions, this article presents only a few of the runs and experiments performed over the 15-mo period of the project at the company's site. More details are available in a project report available from the authors.

Materials and Methods

Membrane Recycle Bioreactor

Figure 1 shows a schematic of the MRB system constructed by Niro Filtration. A jacketed stainless steel tank with a volume of 7000 L (1830 US gal) was used as the fermentation vessel. The system valves, pressure

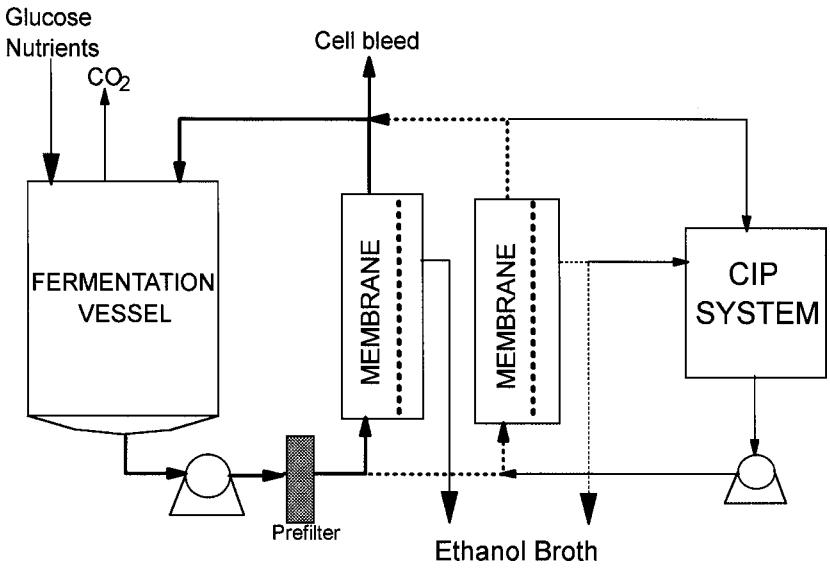

Fig. 1. Schematic of the membrane recycle bioreactor.

gages, and sensors were connected to the programmable logic controller (PLC) (Allen-Bradley, Milwaukee, WI), which had several programs to control the flux by manipulating crossflow rate and transmembrane pressure as needed. Pressure transducers, located at the top and bottom of the tank, were used as a level indicator and controller. This level controller was attached via the PLC to the feed supply valve, which opened and closed depending on the level in the tank.

The fermentation broth was pumped to one of two membrane modules in parallel. All MRB runs reported herein were done with Membralox 19P19-40 modules (U.S. Filter, Warrendale, PA), each containing 3.8 m^2 (40.7 ft^2) of membrane area. Pressure and crossflow velocity to the membrane modules were provided with a centrifugal pump (Fristam, Middleton, WI) rated at 90 m^3/h and 700 kPa. This pump was connected to two in-line horizontal prefilters with 400-μ stainless steel screens to protect the membrane modules.

The membrane modules and the fermentation vessel were connected to a separate clean-in-place (CIP) system that could isolate individual components and automatically clean them when needed. Membrane cleaning was done using the following procedure. The membrane loop to be cleaned was "sweetened off" with water to recover the broth in the loop. Then, tap water at 50°C was flushed through the membrane loop, discarding the permeate and retentate streams. Next, cleaning solution containing 5 g/L of Ultrasil-11 (an NaOH-based cleaner from Ecolab-Klenzade, St. Paul, MN) and 200 ppm of chlorine was recirculated through the loop at 50°C for 30 min. Finally, cleaning solution was flushed out with tap water, and the water flux was measured. If it had not reached the original water flux, cleaning was repeated.

Fermentation

Yeast (*S. cerevisiae*) was obtained from the company's seed fermentors or the main fermentors during their growth phase. The seed culture broth, typically containing 20–25 g of yeast/L, was pumped into the MRB fermentation vessel and concentrated to the required cell density using the membrane modules. After the desired yeast concentration was reached, the glucose feed was started and the process was run continuously. Residence time was maintained by adjusting tank volume and flux.

The glucose feed (corn starch hydrolysate, typically 93–95 dextrose equivalents) and corn steep liquor (CSL) were obtained from the company's supply to their regular fermentation system. Samples of permeate (the MRB outlet) and the fermentation broth from the vessel were analyzed for ethanol and residual sugars by high-performance liquid chromatography and for cell dry wt and total plate count by standard methods *(7)*.

Results and Discussion

Tubular ceramic membranes were selected for this phase of the project because of several advantages: they permit flux management techniques such as backwashing, back-pulsing, and UTP/CPF; they operate in highly turbulent flow conditions; they are made of relatively hydrophilic materials, which minimizes fouling; and they can be cleaned with aggressive chemicals if needed (*[2]*; Filson, J., personal communication; Keefe, R., personal communication). Performance of the membrane is expressed as flux, J (L/[m^2·h]):

$$J = AP_T$$

in which P_T is the transmembrane pressure (kPa) and A is the permeability coefficient (L/[m^2·h]/kPa).

Preconcentration of Yeast

The first task in a run was to grow and preconcentrate the cells to the required cell density. Prior work in our laboratory *(1–3,7)* and elsewhere *(4–6,8)* had indicated that a yeast concentration of about 100 g dry wt/L was necessary to maximize sugar utilization and minimize residence time. Figure 2 shows a concentration run with fermentation broth from the company's main fermentors. A volume of 5600 L with an initial cell concentration (as measured by plate count) of 1.48×10^8 viable cells/mL, equivalent to about 23 g dry wt/L, was pumped into the fermentation vessel. The system was operated at constant transmembrane pressure (140 kPa) and constant flow rate (1350 L/min, equivalent to a crossflow velocity of 5 m/s) with a pressure drop (ΔP) of 140 kPa. Over a period of about 16 h, the flux gradually decreased from 70 to 60 L/(m^2·h). This was a small drop in flux, considering that the fermentation broth was concentrated 4.6X and this fermentation broth contained CSL, which has been shown in previous experiments to cause fouling of the module.

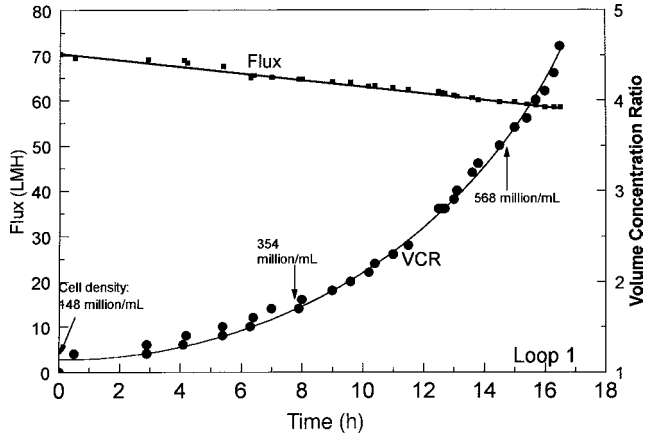

Fig. 2. Preconcentration of yeast cells (run 729). Initial volume, 5600 L; initial cells, 1.48×10^8/mL; transmembrane pressure, 140 kPa; pressure drop (ΔP), 140 kPa; recirculation flow rate, 1350 L/min; temperature, 30°C; LMH, L/(m²·h), VCR, volume concentration ratio.

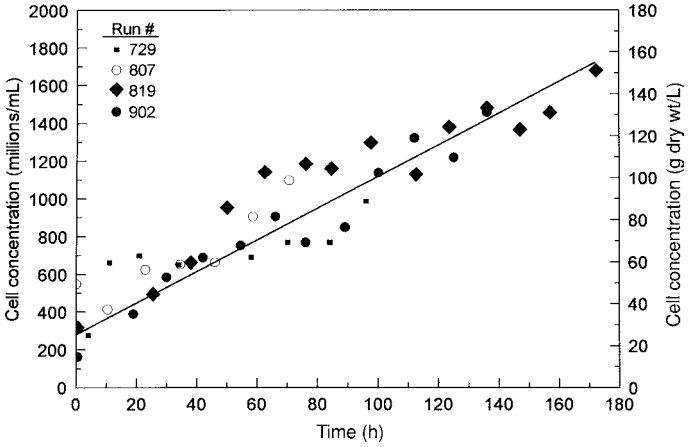

Fig. 3. Cell concentration during MRB runs. Run 819 is expressed as grams/liter, all others as viable cell count in millions/milliliter.

Cell Concentration

Cell concentration in various fermentation runs is shown in Fig. 3. The number of viable yeast cells was $13.5–16.2 \times 10^9$ cells/g of dry yeast, with higher cell concentrations tending to decrease the cell dry wt slightly *(10)*. Because of continuous cell growth, it was necessary to bleed cells to control the viscosity of the fermentation broth and fouling of the module. Cell concentration was maintained below 120 g/L to avoid serious disturbances within the system.

Yeast cell viability, as measured by the methylene blue test, averaged 50–70%. Viability was affected by sugar concentration, initial number of viable cells, and the quantity and quality of nutrients, which should be

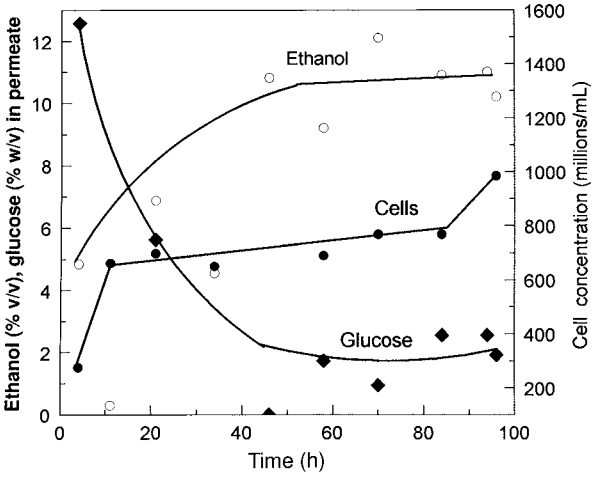

Fig. 4. Fermentation parameters during run 729. Inlet glucose concentration, 210 g/L; residence time, 10 h; temperature, 30°C.

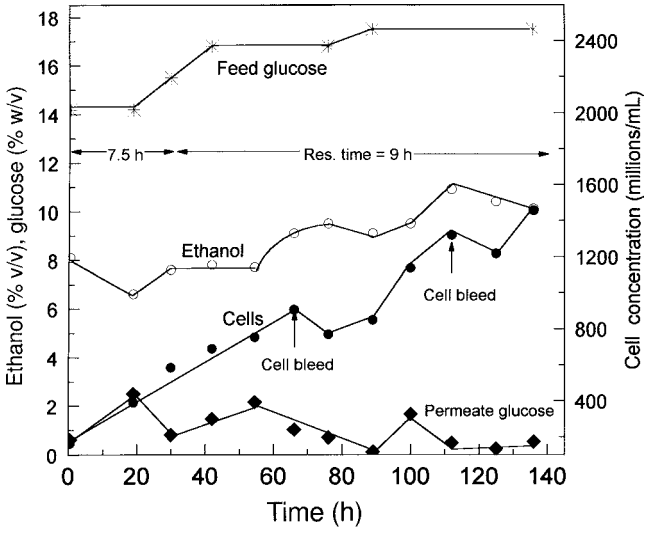

Fig. 5. Fermentation parameters (run 902). Temperature, 31°C.

adjusted for the high cell density. Viability also could have been affected by shear stress from the pumping. With a feed glucose concentration of about 180 g/L, cells reached 6×10^8 viable cells/mL at the end of the preconcentration phase. The higher this value, the better the system performed.

Ethanol Concentration

Ethanol production was directly dependent on glucose concentration in the feed, cell concentration, and residence time, as shown in Figs. 4 and 5. A cell density of about 100 g/L ($1.2–1.5 \times 10^9$ cells/mL) was needed for

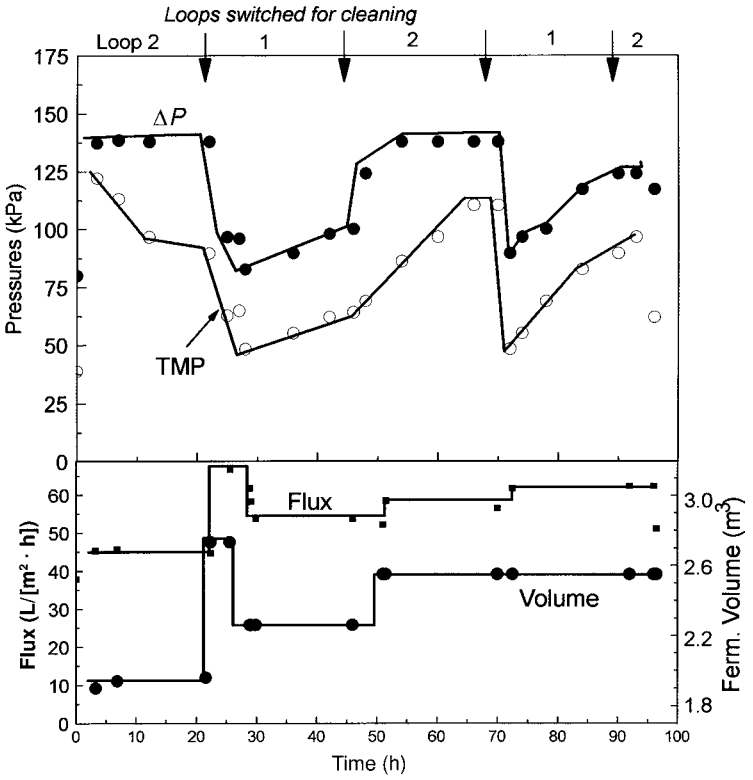

Fig. 6. Membrane parameters during run 729. Recirculation rate for ΔP of kPa, 1350 L/min; residence time, 10 h; temperature, 30°C. TMP, transmembrane pressure.

nearly complete glucose utilization of a feed containing 175 g of glucose/L, resulting in 10.8% (v/v) ethanol and a yield of 0.48 g of ethanol/g of glucose consumed, about 94% of the maximum theoretical value (Fig. 5). Ethanol concentrations varied between 7.5 and 12% (v/v) for feed glucose concentrations of 142–210 g/L.

Membrane Performance

Figures 6 and 7 show selected membrane parameters for the two runs shown in Figs. 4 and 5. Initial experiments were designed to determine those conditions that would provide steady conditions of flux and residence time, which is defined as follows:

$$\text{Residence time (h)} = \text{Volume of fermentation broth in system (L)} / \text{Flow rate through system (L/h)}$$

$$\text{Flow rate (L/h)} = \text{Flux (L/[m}^2\cdot\text{h])} \times \text{membrane area (m}^2\text{)}$$

If flux declined during operation owing to fouling and the pressures could not be adjusted further, the volume was adjusted to keep the residence time at the required value. When the module was clean and brought

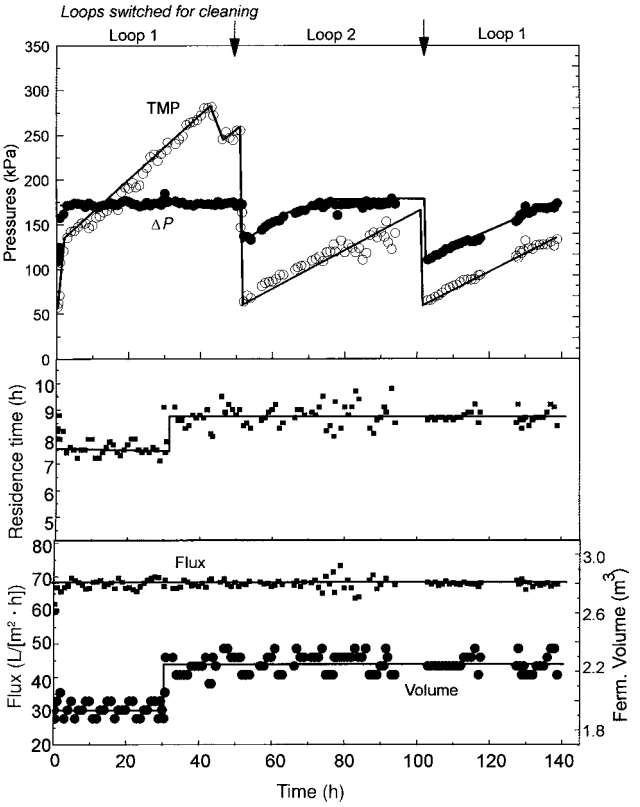

Fig. 7. Membrane parameters (run 902). Recirculation rate, 1450 L/min at ΔP = 172 kPa; temperature, 31°C.

on-line initially, the system transmembrane pressure or crossflow rate (the latter controlled by pressure drop, ΔP) was set very low by the PLC. As the module fouled, these two parameters were gradually increased to keep the flux constant. It was observed that at low fluxes (e.g., below 70 L/[m^2·h]) the system could be maintained for as much as 110 h (~4.5 d) before the transmembrane pressure increased to such an extent (>275 kPa) that cleaning was necessary (Fig. 8). Higher fluxes would require cleanings more often. When cleaning was required, the system switched to the other loop containing the second membrane module.

The stability of the MRB was also affected by gas (CO_2) production. When CO_2 production reached levels above 9.2 g of CO_2/(L·h), the pump experienced large cavitation problems. However, it also appeared that the gas produced was sometimes beneficial in reducing membrane fouling, acting as a scrubber to remove some of the fouling material.

A more serious problem is the presence of antifoaming compounds, some of which can cause serious membrane fouling *(2)*. In one run (no. 819, shown in Fig. 8), some of the antifoam used in the plant's main fermentors inadvertently slipped into the feed stream during the initial stages of the

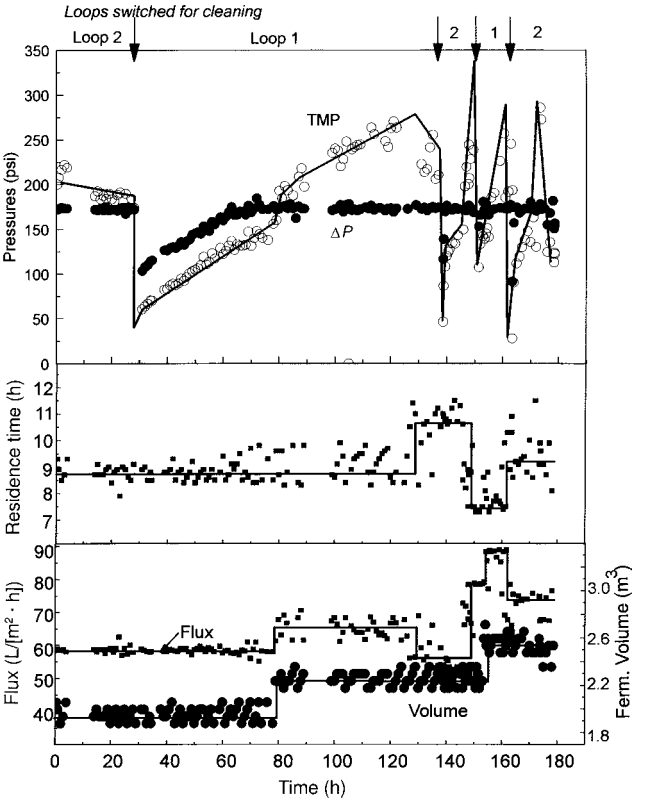

Fig. 8. Membrane parameters for run 819. Recirculation rate, 1450 L/min at ΔP = 172 kPa; temperature, 31°C.

run using loop 2. The normal cleaning cycle was inadequate to remove the antifoam, so that when loop 1 was called back into service after 135 h of operation, the membrane permeability rapidly declined, forcing a steep increase in the rate at which the pressure was increased (30 vs 2 to 3 kPa/h in normal operation).

A separate experiment was performed to evaluate the effect of the antifoam on fouling of the membrane. Many commercial antifoaming agents (e.g., polyoxyethylene polyoxypropylene oleyl ether, polyglycols, silicone oils) severely foul membranes *(2)*. At the time of this study, the company was using a Polaxamer antifoam compound. A sample of the antifoam compound was brought back to the university pilot plant, and a controlled experiment with a model fermentation broth was performed to gage the effect of the antifoam. As shown in Fig. 9, the effect of even a small concentration of antifoam compound on flux was quite pronounced. It is necessary to use nonchemical means of foam control or to use antifoams that have cloud points above the process temperature. Otherwise, the membrane would require frequent and aggressive cleanings.

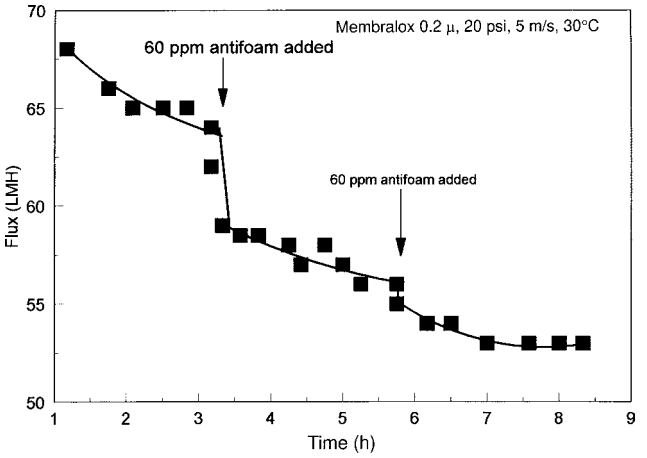

Fig. 9. Effect of Polaxamer antifoam (hydroxy-polyoxyethylene-polyoxypropylene block copolymer) on membrane fouling. Membralox ceramic membrane (1P19-40, 0.2 μ) was used with a model ethanol fermentation broth. LMH, L/(m²·h).

Capital Cost

Table 1 summarizes calculations for capital and operating costs for this application. It was assumed that the same 0.2-μ membrane would be used. However, the newer 60P37-30 (1020 mm long) modules, which contain 60 elements in a single housing, were not available at the time of the trials reported herein. They provide a larger area (21 m^2) for the same cost and are available with smaller-diameter channels—3 instead of 4 mm. This means that for the same crossflow velocity, the volumetric flow rate would be lower with only a slight increase in pressure drop. Based on our data, a crossflow velocity of 5 m/s would require 283 m^3/h of crossflow per module with a pressure drop of about 205 kPa.

Because the MRB probably will be one of the largest ceramic membrane plants in the world, unit membrane cost should be lower than standard catalog prices. The membrane cost (less housing) for this plant was estimated at \$1000/m^2, and the system (including the valves, pipes, fittings, control system, and first set of membranes) was \$1600/m^2. The CIP system would cost an additional \$50,000 for the whole plant, regardless of size (*[2]*; Filson, J., personal communication; Keefe, R., personal communication).

An ethanol plant with a nominal capacity of 3.8×10^6 m^3 (100 million gal)/yr would actually be producing 3.6×10^6 m^3/yr (at the 5% denaturant level). Assuming an 8000-h operating year and ethanol concentration in the permeate outlet of the MRB is 11% (v/v), the flow rate through the MRB, which is permeate flow rate, is

$$\text{Flow rate} = \frac{3.6 \times 10^6 \text{ m}^3 \text{ ethanol/yr}}{8000 \text{ h/yr} \times 60 \text{ min/h} \times 0.11 \text{ m}^3 \text{ ethanol/m}^3 \text{ broth}}$$

$$= 408{,}608 \text{ L/h}$$

Table 1
Cost Analysis of MRB Fermentation System for Ethanol Production

Item	Base case, using data from in-plant trials	Potential with flux management techniques
Fermentation broth volume @ 11% (v/v) ethanol (m^3/h)	408.6	408.6
Volume of tanks needed for 9-h fermentation (m^3)	3677	3677
Cost of tanks at \$2/gal (\$)	1,943,182	1,943,182
Membrane flux (L/[m^2·h])	70	150
Area for MRB (m^2)	5837	2724
Total area (+10% for cleaning) (m^2)	6421	2996
Cost of membranes (\$/m^2)[a,b]	1000	1000
Cost of membrane system (\$/m^2)[a,b]	1600	1800
Cost of membrane system (\$)	10,273,571	5,393,625
Total capital cost (\$)	12,216,753	7,336,807
Capital cost (\$/[m^3·yr] capacity)	32.2	19.3
Number of 60P37-30 modules	306	143
Flow rate per module at 5 m/s (m^3/h)	283	283
Pressure drop per module (kPa)	205	205
Number of parallel flow paths	77	37
Energy consumption (kW/m^2)[a]	1.118	1.118
Energy cost/yr (\$/yr)[a]	2,010,017	938,008
Capital charge (\$/yr)	275,185	171,226
Membrane replacement (\$/yr)	642,098	299,646
Maintenance, labor (\$/yr)	366,503	220,104
Cleaning cost (\$/yr)	44,947	89,894
Operating cost (\$/yr)	3,338,749	1,718,878
Operating cost		
(\$/m^3 ethanol)	9	4.5
(\$/gal ethanol)	0.034	0.017

[a]Ref. 2.
[b]Filson, J., personal communication; Keefe, R., personal communication.

Assuming a flux of 70 L/(m^2·h), membrane area = 408,608 L/(h·70 L/[m^2·h]) = 5837 m^2. With 10% extra needed for cleaning, this comes to 6421 m^2. The membrane system cost = \$1600/m^2 × \$6421 m^2 = \$10.27 million.

Assuming a 9-h residence time, the total volume of tanks required would be 408,608 L/h × 9 h = 3677 m^3. At a cost of \$528/m^3 (\$2/gal), the cost of fermentation tanks is \$1.94 million (Keefe, R., personal communication; Gadomski, R. T., personal communication). Thus, the total MRB system cost is \$10.27 million + \$1.94 million + \$50,000 for the CIP system = \$12.22 million. This is equivalent to \$32/(m^3·yr) of ethanol capacity (\$0.122/[gal·yr]). Since a typical corn wet-milling plant of this capacity would cost at least \$250 million to construct (Gadomski, R. T., personal communication), the MRB would be 5% or less of the plant cost.

Operating Costs

Operating costs are based on energy (electric power for recirculating pumps), membrane replacement, depreciation, cleaning, and labor/maintenance. Under the operating conditions of the MRB, the Membralox modules have a unit energy consumption of 1.118 kW/m^2 *(2)*. Assuming a power cost of \$0.035/kWh, energy cost per year = 1.118 kW/m^2 × 6421 m^2 × 8000 h/yr × \$0.035/kWh = \$2.01 million/yr.

The capital charge, which provides for depreciation, insurance, and so forth, was calculated based on a depreciation over a 14-yr period. Membrane costs are not included in this category and are considered a separate operating expense. In this case, system cost less membranes = \$1600 – \$1000 = \$600/m^2. Using a 14-yr straight-line method of depreciation

$$\text{Depreciation} = \$600 \times \$6421/14 = \$275{,}185/\text{yr}$$

Membrane replacement costs are based on a 10-yr life. Membralox membranes have been in commercial service since 1984, and 10-yr or more lifetimes are now being recorded for such relatively nonaggressive applications (Filson, J., personal communication). Thus, membrane replacement cost = \$1000/m^2 × \$6421 m^2/10 yr = \$642,098/yr. Labor and maintenance are charged at a nominal rate of 3% of installed cost, which in this case is \$366,503/yr.

For cleaning cost, conventional detergents and sanitizers can be used. A detailed analysis at the plant site indicated that it would be about \$7/(m^2·yr) = \$44,947/yr. This includes the additional power needed during the 1-h cleaning cycle.

The total operating cost is \$3.34 million/yr. This is equivalent to \$9/m^3 of ethanol produced in the plant (\$0.034/gal). The highest costs are power requirements (60% of operating costs) and membrane replacement (20%).

Potential to Reduce Costs

Capital costs can be reduced by using polymeric membranes. However, their lower capital cost has to be balanced against the lower flux and more frequent replacement of membranes. Increasing flux will reduce the membrane area as well as capital and operating costs. This can be done in the following ways. First, the flux we used for our calculations (70 L/[m^2·h]) is based on run 902 (*see* Fig. 7). Higher transmembrane pressure will increase the flux. However, it will increase the cleaning frequency from every 4 to 5 d to perhaps a daily cleaning. Considering that the cleaning cost right now is so low, the cost-benefit ratio would favor more frequent cleanings if the flux can be increased. Second, overall flux could also be increased by using back-pulsing or the CPF/UTP mode *(2,11,12)*. Back-pulse devices typically add about 9–18% to the cost of a module. Although these devices and techniques need to be confirmed for this large-scale application, there are several successful industrial applications that use these techniques (Filson, J., personal communication; Keefe, R., personal communication).

Incorporating these factors could increase flux to 150 L/(m^2·h). The added cost for the back-pulse devices increases capital cost to \$1800/m^2, but the total capital cost is reduced to \$7.34 million and operating cost is reduced by 50% (Table 1). If cheaper membrane modules are used and assuming the flux remains the same with fluid management and back-pulse techniques, the capital cost could decrease even further with an additional reduction in operating cost.

Conclusion

The on-site trials demonstrated that the MRB is a practical concept from a technical viewpoint. One additional advantage of this type of fermentor that became apparent in the plant was that the product stream (the permeate) was clear and contained no suspended matter. This could essentially eliminate the centrifuges needed to process the "stillage" and improve the heat transfer in the beer still and distillation columns. There should be a reduction in energy consumption and in waste treatment costs. None of these factors were specifically included in the cost estimates. The MRB will bring considerable benefits to ethanol production and other fermentations that need higher cell concentrations and productivities.

Acknowledgments

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