Membrane Filtration of Corn Steep Water

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ABSTRACT

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Membrane filtration is a cost-effective alternative to heat pasteurization of corn steep water. Trials were done in an operating ethanol plant with commercial spiral-wound modules. Flux increased with transmembrane pressure and became independent of pressure at >10 psi (69 kPa) with flux being higher at higher cross-flow velocities. Average flux at 4× concentration factor over 24-hr operating cycles was 34 L/m^2/hr under optimum conditions. Capital cost of the membrane system is expected to be lower because it eliminates the heat pasteurizer and centrifuge and reduces cooling requirements. Operating cost of the microfilter are about one-third of a heat pasteurization system and provides the opportunity to recover insoluble protein and starch for use in corn gluten feed. Microfiltered steep water could improve ethanol fermentation efficiency and reduce fouling of heat exchangers in the fermenters, beer still, and steep evaporators.

In corn wet milling, corn is steeped in water (usually process return water or starch wash water) at ≈50°C for 30–60 hr. Steeping softens the corn kernel, allowing easier separation of corn germ, gluten, fiber, and starch. During steeping, soluble proteins and other organic matter leach out of the corn into the steeping solution, and lactic acid is formed due to the growth of lactic acid bacteria. After steeping, the steep water is withdrawn from the steep tanks. It typically contains 9–16% (w/v) total solids, of which 37–40% is nitrogen-containing matter (protein), 8–10% is soluble carbohydrate (sugars), and 15–20% is lactic acid (May 1987; Wu 1988). It also contains sulfur dioxide and phytic acid and sometimes also contains starch and insoluble protein from broken kernels. The microbial load of steep water is high (1 to 5 × 10^4/mL).

Typically, 4–6 gallons of steep water are produced per bushel of corn in corn wet mills. The steep water is evaporated to ≈50% total solids before being added to the corn gluten feed stream, which is then dried. Higher solids levels in the concentrated steep liquor would be desirable, but it is difficult due to fouling of the evaporator heat exchangers by the suspended solids in the steep water. Biweekly boilouts with alkali are common with certain evaporators to remove fouling deposits (May 1987). In the fuel ethanol and pharmaceutical industries, steep water has been used for many years as a nutrient in fermentation (Liggett and Koffler 1948). It is rich in amino acids, minerals, and vitamins, and also contains other nitrogen compounds which may be useful for microbial growth (Christianson et al 1965) and in poultry diets (Wright 1987). However, due to the high microbial load, the steep water is usually heated to sterilize or pasteurize it before using it in the fermenters. This is also a troublesome operation due to the fouling of the heat exchangers. The high heat could also denature and destabilize protein and gelatinize starch which could eventually pass into the fermenter and to the postfermentation downstream operations such as the beer still, causing further operational difficulties. A separation step (centrifugation) is usually required to reduce suspended solids before pasteurization.

Cross-flow membrane filtration with synthetic semipermeable membranes is a possible single-step solution to these problems. Microfiltration (MF) or ultrafiltration (UF) is an extremely effective method of clarification and sterilization which uses substantially less energy than the current operations (Cheryan 1998). Membranes are increasingly used in corn wet-milling plants as an efficient and cost-effective method of replacing many conventional wet-milling unit operations (Singh and Cheryan 1997a,b). Ray et al (1986) concentrated steep water from 6 to 12% using a hollow fiber reverse osmosis (RO) module after prefiltration with a screen filter. At 50°C and a pressure of 400 psi, flux was 4.5–9 L/m^2/hr (LMH). Based on this data, Gienger and Ray (1988) developed a hybrid process (RO + evaporation) that could substantially lower energy requirements for concentrating steep water.

Wu (1988) reported on the UF and RO of steep water. The steep water was precentrifuged to remove suspended matter. Flux with a 1,000 molecular weight cutoff (MWCO) polysulfone and cellulose acetate membranes was low, typically 7–9 LMH at room temperature. The UF permeate was then concentrated by RO at 1,000 psi, resulting in initial flux of 19 LMH, which dropped to 3.5 LMH within a few hours. Of the water in the original steep water, ≈80% was recovered (a net fivefold concentration by RO and UF). Permeate quality from both were acceptable enough to be discharged from the plant. The common key factor in both these studies was the removal of suspended solids before UF or RO to minimize fouling of the membranes.

Our objective in this work was to evaluate the feasibility of sterilizing and clarifying steep water by microfiltration. In this particular project, the goal was to use the microfiltered steep water for ethanol production; therefore, it was important to compare the fermentation efficiency (ethanol yield and rate of ethanol production) between membrane-filtered steep water and heat-pasteurized steep water. Membranes are also being used extensively in downstream processing after fermentation (Cheryan and Mehaia 1986; Cheryan 1998; Singh and Cheryan 1998); therefore, the beneficial effect of microfiltration on a membrane operation in fermentation was also studied.

The work was conducted in two locations. Preliminary experiments were done in our laboratory with model systems and steep water from a corn wet-milling ethanol plant. Benchtop and small, pilot-scale equipment was used to determine the ranges of important operating variables, to select the most appropriate membrane in terms of performance (membrane flux, rejection of suspended solids), and to determine potential cost of the commercial membrane system. The data were also used to design and construct the pilot plant that was subsequently used on site at one of the largest corn wet milling ethanol plants in the world to test this concept. This article describes the pilot plant work.

MATERIALS AND METHODS

Equipment

A standard commercial 4-in. spiral-wound module with an 80-mil spacer was obtained from Advanced Membrane Technology (AMT, San Diego, CA). Its nominal dimensions were 9.7 cm in diameter and 99 cm in length (3.8 × 38 in.) with an effective area of 3.72 m^2 (40 ft^2). The membrane was polyvinylidene fluoride (PVDF) with a nominal MWCO of 500,000. A schematic of the pilot plant as

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installed in the ethanol plant is shown in Fig. 1. The steep water from the plant's steep tanks was prefiltered through a 100-mesh screen strainer and entered the 30-gallon feed tank through a mechanical float valve that kept the level in the tank constant. The feed was pumped by a centrifugal pump (DCH2, 3 by 2.5 in., 256J, 15 HP; Ampco Pumps, Milwaukee, WI) through the membrane module. When operated in the batch concentration mode, the retentate was recycled back into the feed tank (valves V5 and V6 were closed and V7 was open). When operated in the feed-and-bleed mode, the retentate was recycled back to the pump inlet (valve V5 was open and V7 closed). A portion of the retentate could be bled through a ball valve (V6) at the required flow rate to maintain the desired concentration factor.

When the pump was turned on, the module inlet (V3) and outlet (V4) valves were slowly opened to achieve the required cross-flow rate (Q), pressure drop (ΔP), or both across the module. After stabilizing the flow and pressures, the concentrate bleed valve (V6) was then set manually to maintain a particular concentration factor. The concentration factor (X) is defined as:

$$X = \text{Feed flow rate/retentate flow rate} = (\text{retentate flow rate} + \text{permeate flow rate})/\text{retentate flow rate} \qquad (1)$$

Transmembrane pressure (P_T) and pressure drop (ΔP), respectively, are defined as:

$$P_T = 0.5\,(P_i + P_o) - P_p \qquad (2)$$

$$\Delta P = P_i - P_o \qquad (3)$$

where P_i is inlet pressure (measured with gauge P1, Fig. 1), P_o is outlet pressure (P2) on the retentate side, and P_p is permeate back pressure (P3). For this particular module, little or no permeate back pressure was allowed. The permeate line was open to the atmosphere, and P_p in Equation 2 was 0.

The relationship between ΔP and cross-flow rate (Q) for this module was experimentally determined in our laboratory at 120°F (49°C):

$$Q = B\,(\Delta P) \qquad (4)$$

If Q is in gallons per minute (gpm) and ΔP is in psi, the coefficient, B, is 3.8 gpm/psi. If Q is in liters per minute (lpm) and ΔP is in kPa, B = 2.09 lpm/kPa. The manufacturer recommended that ΔP not exceed 10 psi (69 kPa), which limited the maximum flow rate to 38 gpm (144 lpm).

Flux (the permeate flow rate) was determined with a graduated cylinder and stop watch. It is expressed as LMH and defined as:

$$\text{Flux } (J), \text{ LMH} = \text{permeate volume rate (L/hr)/membrane area (m}^2) \qquad (5)$$

Membrane Cleaning

At the end each run, the membrane was thoroughly cleaned using the principles described by Cheryan (1998). First, the entire system was flushed with softened water, discarding the permeate and retentate streams until these streams appeared visually clean. Second, the cleaning solution (0.25–0.50% Ultrasil-11, a trade name for a NaOH-based cleaner from EcoLab/Klenzade, St. Paul, MN) was circulated through the system. The retentate was recirculated back to the tank during the cleaning cycle. The cleaning solution was pH 10.5–11 and at 50°C. Third, after 30 min of cleaning, the system was flushed out with fresh softened water. The water flux was then measured under standard conditions. If the original clean water flux was not obtained, this cleaning was repeated.

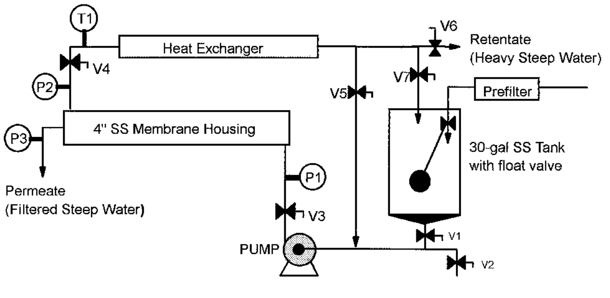

Fig. 1. Steep water membrane filtration pilot plant.

Fermentation Efficiency

Ethanol fermentation efficiency of membrane-sterilized steep water was compared with the heat-pasteurized steep water. The fermentations were done in 1,000-mL Erlenmeyer flasks at 30°C in several replicates. The fermentation medium was composed of 300 mL of fermenter supply from the plant (containing hydrolyzed corn starch at ≈92 dextrose equivalence [DE] and with a total solids of 27.5% w/w), 50 mL of phosphate buffer (pH 6), 50 mL of steep water (membrane sterilized or heat pasteurized) and 0.5 mL of liquid ammonia (10–12% w/v). The yeast inoculum was obtained from the first stage of the company's multiple stage fermentors. The cells were centrifuged and washed twice with sterile phosphate buffer (pH 6) solution. The yeast inoculum level was 20% (≈20×10^6 cells/mL). After inoculation, the ethanol fermentation was conducted for 20 hr on a rotary shaker at 150 rpm at 30°C.

Analytical Methods

Total solids (TS) were measured by gravimetric analysis. A preweighed sample was dried on a steam table for ≈1 hr, then placed in a vacuum oven for 1 hr. Ethanol and dextrose were measured by HPLC using a BioRad HP-87X fermentation monitoring column. Cell dry weight was obtained by centrifuging a sample of the fermentation broth at 3,000 × *g* for 20 min, discarding the supernatant, resuspending the pellet in phosphate buffer (pH 6), centrifuging, drying the pellet, and determining its weight. Total plate count was determined by standard methods (Pekin Energy Co.).

RESULTS AND DISCUSSION

Water Flux

Typical water flux data for the spiral polymeric membrane is shown in Fig. 2. Two temperatures (90°F/32°C and 120°F/49°C) and three pressure drops (2, 4, and 6 psi) were evaluated. The relationship between flux and transmembrane pressure (Cheryan 1998) is:

$$J = A \bullet P_T \qquad (6)$$

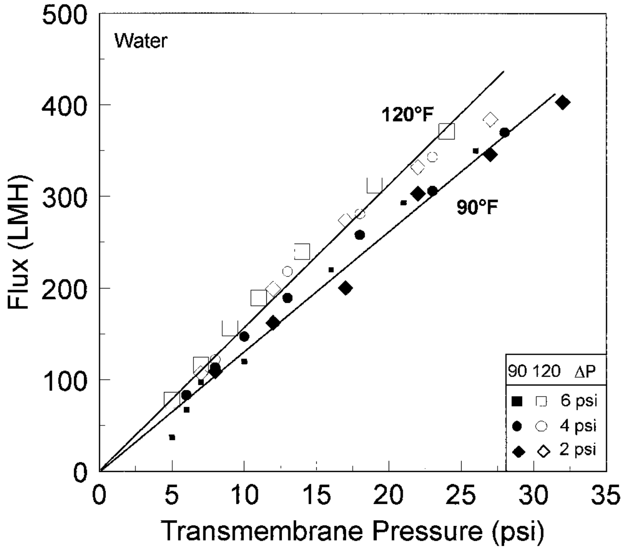

Fig. 2. Water flux of spiral membrane module. Effect of temperature, transmembrane pressure, and cross-flow rate (expressed as pressure drop). Open symbols = 120°F, closed symbols = 90°F.

where *A* is the membrane permeability coefficient, defined as:

$$A\ (\text{LMH/bar}) = \text{Flux (LMH)}/P_T(\text{bar}) \qquad (7)$$

where 1 bar = 14.5 psi.

As expected for water, no polarization effects were observed and flux was directly proportional to P_T, as shown in Equation 6. The membrane permeability coefficient (*A*) with water was 191 LMH/bar at 90°F, and 210 LMH/bar at 120°F. These values are in the range specified by the membrane manufacturer (AMT, San Diego, CA).

Steep Water

The first set of experiments were conducted in the total recycle mode in which the permeate and retentate were recycled back to the feed tank. Initially, the system was operated in a batch concentration mode until the required concentration factor was reached and then it was operated in the total recycle mode. In a run at a concentration factor of 2×, 120°F/49°C, P_T of 8 psi (55 kPa) and ΔP of 4 psi (28 kPa), a steady permeate flux of 31 LMH was obtained (Fig. 3A). Pressure excursion studies after 24 hr of membrane processing are shown in Fig. 3B. Flux becomes independent of transmembrane pressure at ≈10 psi (69 kPa) and a significant effect of cross-flow rate (expressed as pressure drop) was observed. This behavior is typical of systems displaying concentration polarization effects (Cheryan 1998). The rate at which rejected solutes accumulate on the membrane surface due to convective flow is balanced by the rate at which solids are removed by shear or turbulence due to the cross flow. Increasing pressure merely brings more solids to the surface, resulting in a thicker layer and canceling out the benefits of higher pressure on flux.

Similar behavior was observed at higher concentration factors of 3× and 4× (Fig. 4). In fact, P_T values higher than the optimum caused a decrease in flux, with the decrease being greater at lower cross flow due to greater polarization (Fig. 4B). This decrease could be due to an increase in flow resistance due to compression of the polarized gel layer at higher pressures, or due to an increase in osmotic pressure at the membrane surface which increases exponentially at high solute concentrations. Either one of these mechanisms could cause a disproportionate increase in the resistance to permeate flow through the membrane.

In the feed-and-bleed mode, fresh feed is processed continuously and the permeate and retentate are not recycled but are removed from the system. Microfiltration of steep water in a feed and bleed mode at 3× and 4× is shown in Fig. 5. Average flux of 30 LMH was obtained in both 3× and 4× feed-and-bleed operations at a P_T of 11 psi (76 kPa) and ΔP of 8 psi (55 kPa), equivalent to *A* values of 39.5 LMH/bar. Flux remained fairly stable for 30 hr without cleaning. The pressure excursion studies done at the end of the runs (Fig. 5B) showed results similar to those of the total recycle mode. Optimum conditions appear to be P_T 11–15 psi (76–103 kPa) and ΔP 8 psi (55 kPa) to give an average flux of 34 LMH.

The permeate quality was excellent. No traces of suspended matter (as observed visually) or microorganisms (as measured by standard plate counts) were evident in any of the runs, confirming the effective sterilizing and excellent clarification capabilities of microfiltration. Steep water solids in the feed averaged 9.5% w/w,

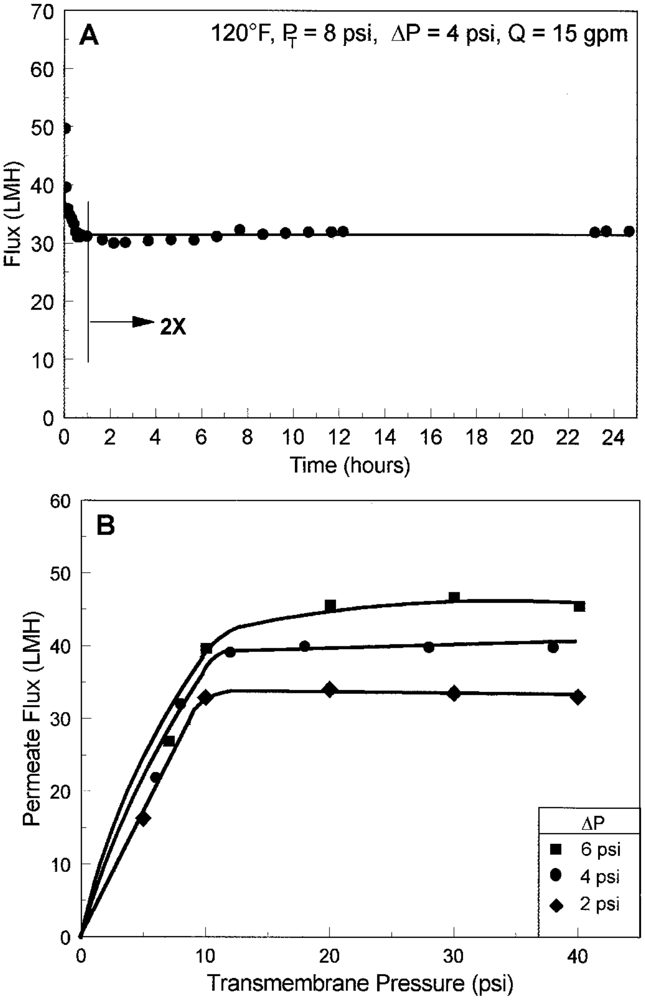

Fig. 3. Microfiltration of steep water in total recycle mode at 2×. **A,** Fouling study. **B,** Effect of transmembrane pressure and cross-flow rate on flux. Data taken at the end of the run is shown in A.

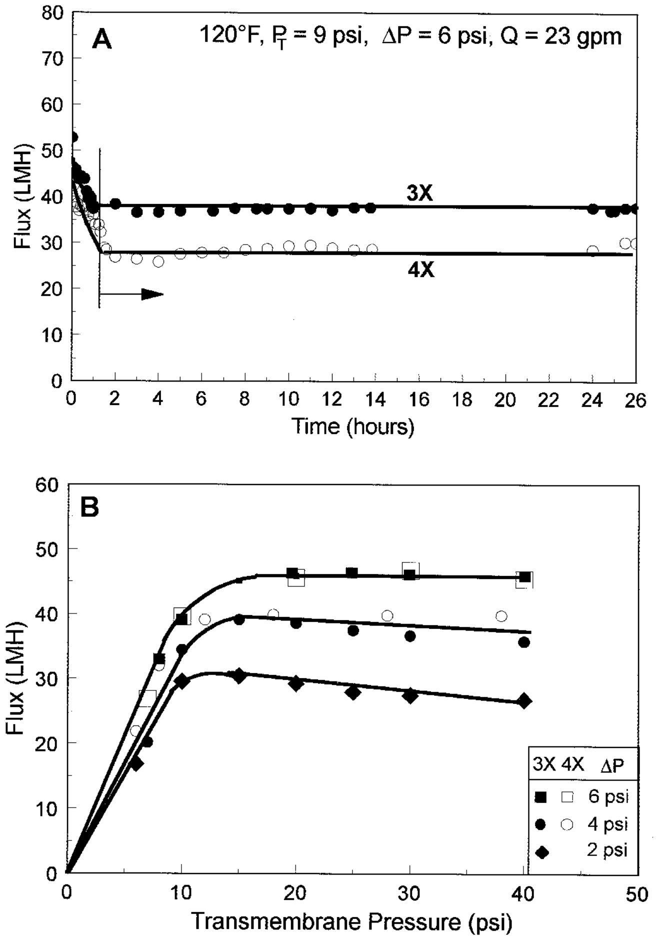

Fig. 4. Microfiltration of steep water in total recycle mode at 3× (closed symbols) and 4× (open symbols). **A,** Fouling study. **B,** Effect of transmembrane pressure and cross-flow rate on flux. Data taken at the end of the runs shown in A.

permeate solids averaged 9.0% w/w, and retentate solids were 11% at 4×.

Fermentation Efficiency

Heat-pasteurized steep water from the plant (pasteurized at 260°F for 1 min) and membrane-filtered steep water (from the feed-and-bleed run at 4×, Fig. 5) are compared on ethanol fermentation parameters (Fig. 6). The membrane-filtered steep water gave comparable or slightly better ethanol concentration (7.74%, w/w) compared with heat-pasteurized steep water (7.12%, w/w ethanol). The rate of glucose consumption by the yeast was almost the same. Yields in both cases were ≈0.50 g of ethanol per gram of glucose, which is close to theoretical. This shows that microfiltered steep water is an as good or better nutrient source than heat-pasteurized steep water for ethanol fermentation.

Effect of Steep Water Microfiltration on Membrane Performance

In many fermentation operations, membranes are used as the first downstream step (to harvest or to separate the microbial cells) and, in some cases, to recycle the cells to the fermenters (Cheryan and Mehaia 1986; Cheryan 1998; Escobar et al 2001). However, steep water can foul these membranes also, as shown in the microfiltration of a model fermenter feed with a ceramic membrane (USFilter Membralox 1P19-40, 0.2 µm) (Fig. 7). The feed contained starch hydrolyzate at the equivalent of dextrose at 220 g/L, heat-pasteurized steep water at a concentration of 11.5%, and yeast at 45 g/L (the steep water and starch hydrolyzate were obtained from the ethanol company). The goal was to maintain a minimum flux of 70 LMH. At steady state, this required a P_T of 86 psi (593 kPa) to maintain a flux of 70 LMH at 90°F. This is equivalent to a permeability coefficient of 11.8 LMH/bar.

A similar trial was performed with microfiltered corn steep liquor in the feed stream (Fig. 8). A flux of 80 LMH or more could be maintained with an increase in the P_T from 25 psi (172 kPa) to 51 psi (352 kPa), giving a final permeability coefficient of 22.7 LMH/bar,

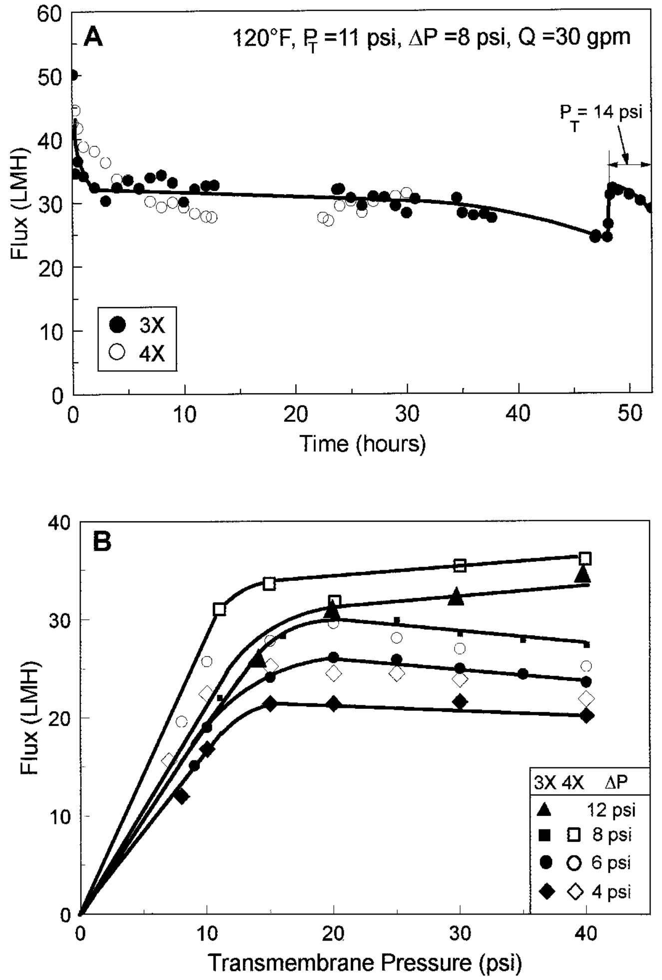

Fig. 5. Microfiltration of steep water in feed-and-bleed mode at 3× (closed symbols) and 4× (open symbols). **A,** Fouling study. **B,** Effect of transmembrane pressure and cross-flow rate on flux. Data taken at the end of the runs shown in A.

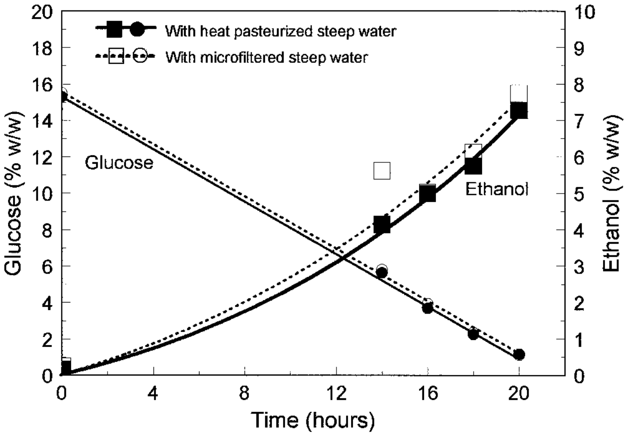

Fig. 6. Ethanol production by fermentation of hydrolyzed corn starch with yeast. Comparison of heat-pasteurized with microfiltered steep water.

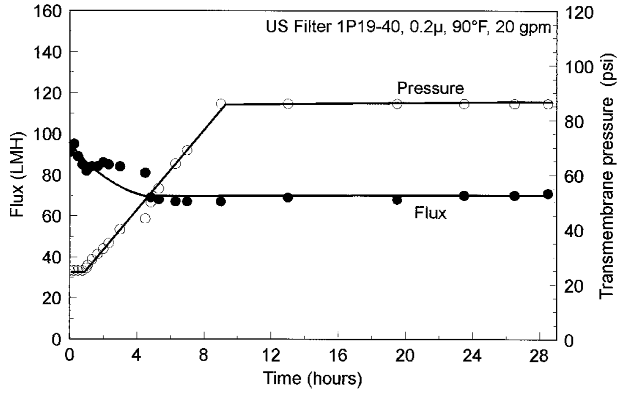

Fig. 7. Performance of USFilter ceramic membrane module with model fermenter feed containing 11.5% heat-pasteurized steep water, 72.5% starch hydrolyzate, 11.5% water, and 4.5% yeast (20 gal/min = 5 m/sec cross-flow velocity).

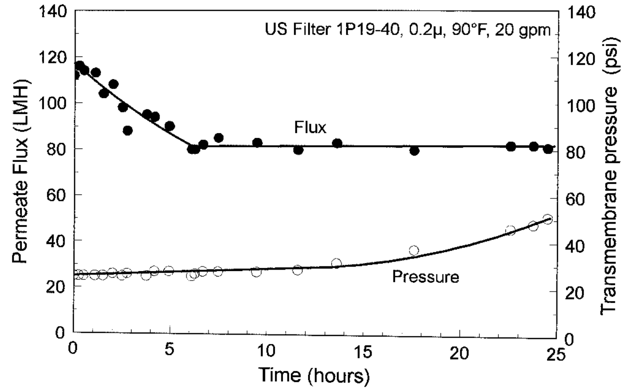

Fig. 8. Performance of USFilter ceramic membrane module with model fermenter feed containing 11.5% microfiltered steep water, 72.5% starch hydrolyzate, 11.5% water, and 4.5% yeast (20 gal/min = 5 m/sec cross-flow velocity).

almost double the value with the unfiltered steep water. This is another benefit of microfiltration of steep water.

Economic Analysis

An estimate of the costs of membrane filtration versus heat pasteurization was made based on plant capacity of 100 million gallons of ethanol per year (380,000 m^3 per year); pasteurized steep water required for fermentation is 200 gpm (45,432 L/hr); steep water available in the plant at a flow rate of 267 gpm (60,651 L/hr) at 120°F/49°C (this results in a concentration factor of 4); steep water total solids of 9.5% w/w and permeate solids of 9.0% w/w; membranes cleaned every 24 hr for 2 hr (thus, the estimated membrane area will increase by a factor of 24/22 to account for the cleaning time); and average flux for the 24-hr cycle of 34 LMH. The membrane area needed = (45,432 L/hr/34 LMH) × (24/22) = ≈1,460 m^2. Assuming a total membrane plant cost of \$300/m^2 for an industrial system, including the first set of membranes (Cheryan 1998), the total capital cost will be \$438,000 for a complete skid-mounted membrane plant.

Annual operating costs of the membrane system were calculated assuming an operating year of 8,760 hr as power consumption for spiral modules operating under the specified conditions and with a pump efficiency of 50% = 0.05 kW/m^2 (Cheryan 1998); power cost ≈\$0.04/kWh = \$ 25,600/year; maintenance at 3% of fixed capital investment = \$ 13,140/year; membrane replacement (1-year life at \$50/m^2) = \$ 73,000/year; annual cleaning cost (Cheryan 1998) = \$10,200/year. Total operating cost for membrane plant = \$121,940/year = 0.122 cents per gallon of ethanol.

The present operating cost of heat pasteurization was determined as steep water (45,432 L/hr or 100,132 lb/hr) was heated from a steep tank temperature of 120°F/49°C to 260°F/126.7°C. Heat required (100,132 lb/hr × 1 Btu/lb°F × 140°F) = 1.4×10^7 Btu/hr; steam required at 1,000 Btu/lb of steam = 14,000 lb of steam per hour. If steam is produced in a cogeneration plant, steam cost at \$2/1,000 lb of steam = \$28/hr or \$245,280/year.

Power requirements were a pasteurizer pump that required 24 kW and a steep water centrifuge that required 48.5 kW; power cost at \$0.04/kWh is \$25,400/year. Maintenance requirements included pasteurizer maintenance cost of \$6,000/year and centrifuge maintenance cost of \$60,000/year, for a total maintenance cost of \$66,000/year. Cleaning cost was \$10,000 per year. Therefore, total operating cost for heat pasteurization = \$346,680/year.

Not included in the cost estimates are depreciation or cooling requirements. For example, the heat-pasteurized steep water has to be cooled from 260°F to the fermentation temperature of 86–92°F/30–33°C. The microfiltered permeate has to be cooled only from 120°F/49°C; therefore, its cooling cost should be less. In addition, the benefit of reduced fouling by the microfiltered steep water in steep evaporators is expected to be substantial (G. C. Liaw, *personal communication*) and has not been included; neither has the possible beneficial effects on fermentation efficiency.

Another point to consider is the value-added benefit of retentate solids from the microfilter. This stream contains protein and starch which could be used in corn gluten meal, as suggested by Liaw et al (1998). They describe a similar process for membrane filtration of steep water operated at higher concentration factors of 10–25× to increase the protein content of the retentate solids to 60%. They estimated such a process would recover 0.2–0.3 lb of corn gluten meal solids per bushel of corn. For the case study considered here, a 100-million-gallon/year ethanol plant would process 38 million bushels/year. This translates into an annual recovery of 8–10 million lb of corn gluten meal solids. At corn gluten meal prices of \$180–240/ton, this means an additional revenue of \$0.7–1.2 million/year. If this recovery is included in the cost analysis, the payback period even to replace an existing heat pasteurization system is ≈6–12 months.

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