0273-2289/99/77–79/0485/$13.75

Electrodialysis of Acetate Fermentation Broths

U. N. Chukwu and M. Cheryan*

Agricultural Bioprocess Laboratory, University of Illinois,
1302 W. Pennsylvania Avenue, Urbana, IL 61801,
E-mail: mcheryan@uiuc.edu

Abstract

Electrodialysis (ED) shows good potential for downstream processing of acetate fermentation broths, to separate acetic acid while unreacted glucose and other nutrients are partially recycled back to the fermenter. With conventional anion- and cation-exchange membranes, higher current increased acetate flux, water flux, and energy consumption. Multiple ED stacks connected in series with unequal initial volumes for a batch process maximized acetate concentration in the concentrating stream to 134 g/L calcium-magnesium acetate (CMA) in the fermentation broth at pH 6.8. Back-transport of acetate from the product into the feed stream and water transport limit the maximum concentration possible. Cost of ED is about $295/ton acetate for the CMA broth.

Index Entries: Acetate; electrodialysis; membranes; separation.

Introduction

Acetic acid is an important commodity chemical with a U.S. production of about 4 billion lbs/yr, representing a market value of $1.2 billion. Much of it is petroleum-derived and converted into acetates, e.g., polyvinyl acetate, sodium acetate, potassium acetate, calcium magnesium acetate (CMA), and acetate esters. Acetate can also be produced by aerobic fermentation of ethanol (the vinegar process) or by anaerobic fermentation of dextrose by *Clostridium thermoaceticum (1–3)*. The feedstock (e.g., dextrose) and downstream processing are a major portion of the manufacturing cost. Membrane technology can be used in most phases of downstream processing. Microfiltration (MF) and ultrafiltration (UF) are effective for separation and recycle of the cells *(4–6).* Nanofiltration (NF) has been used to separate organic acids (depending on the degree of dissociation) and monovalent salts from sugars and other organic compounds *(7–9).* We reported the use of electrodialysis (ED) with lactic acid *(10,11)* and with vinegar *(12)*, which is a low-pH acetic acid-fermentation broth. This article

*Author to whom all correspondence and reprint requests should be addressed.

reports on the application of ED for the separation, purification, and concentration of acetates from high-pH fermentation broths. Initial studies were conducted with model solutions of reagent-grade acetic acid neutralized to various pH values with sodium hydroxide or dolomitic lime (to simulate a CMA broth) to establish the operating range of several process parameters. The process was then optimized with real CMA fermentation broths.

Materials and Methods

Equipment

A bench-top ED unit was used (Medimat 220, Ionics Inc., Watertown, MA). It contained 20 cation-exchange membranes (CR61 CZL-386) and 20 anion-exchange membranes (AR103 QZL-386). These are standard desalting membranes used in a variety of food and industrial applications; information on their properties is available from the manufacturer. Total effective membrane area was 0.46 m^2. The power supply unit (TCR 80 S13, Electronic Measurement, Inc., Neptune, NJ) provided 0–80 volts and 0–15 amps. An electrode stream consisting of 0.2 *N* sodium sulfate acidified to pH 2.0 circulated at a flow rate of 500 mL/min to remove gases formed at the electrodes during ED. Hold-up volume within the stack was 0.46 L for each of the concentrating (C) and diluting (D) streams. Membranes were cleaned at the end of experiments with NaOH and ethanol solutions as recommended by the manufacturer.

Feed Solutions

Model acetate solutions were prepared by diluting glacial acetic acid (100% acetic acid; Baker's Chemicals, Phillipsburg, NJ) with deionized water to the required concentration and then titrating with 10 *N* sodium hydroxide to pH 5.6 or 6.8. Model CMA solutions were made by neutralizing with dolime (high-magnesium calcium oxide) to pH 6.8. Glucose was added to some of the model solutions at 5 g/L to simulate incompletely converted fermentation broth. The CMA model solution was filtered through Whatman filter paper to obtain a clear solution prior to ED.

The CMA fermentation broth was prepared in our laboratory as described earlier *(1–3,5,6)*. Dextrose was fermented in the presence of yeast extract and other nutrients by *Clostridium thermoaceticum* using dolime as the neutralizing agent during the fermentation. Prior to use in the ED equipment, the broth was clarified using a 0.2 μ ceramic microfiltration module (Ceramem Separations, Waltham, MA).

Procedure

All experiments reported in this were conducted in the batch recycle mode. The objective was to determine the effect of current and feed concen-

tration on energy consumption and flux of acetate and water. The ED membrane stack was equilibrated for each experiment by circulating a small volume of the feed at 1.8 L/min at 0.25 amps of current for at least 20 min. This volume was then discarded and the feed was introduced into the feed compartment of the ED stack, also known as the diluting stream (D-stream). The parallel concentrating (C) stream (C-stream) was either the same feed or water. Current was applied after 2 min of circulation and held constant for the duration of the experiment. Temperature of ED experiments was 24°C.

Samples of 5–10 mL were taken from each stream at regular time intervals during the course of an experiment. Each experiment was run at least twice on separate days. Reproducibility was excellent *(12,14)* and average values are reported.

Analytical Methods and Presentation of Data

Concentrations of acetic acid and glucose were measured by HPLC using the BioRad HPX-87H fermentation monitoring column *(5–7)*. Cell concentrations were measured by gravimetric analysis. Unless otherwise mentioned, the concentration of acetate is reported in terms of acetic acid. An acetic acid concentration of 1 g/L is equivalent to 1.225 g/L of CMA and 1.375 g/L of sodium acetate. Minerals (Na, K, Ca, Mg) were measured by atomic absorption as practiced in the Microanalytical Laboratory, Department of Chemistry, University of Illinois (Urbana, IL).

1. Acetate flux is expressed as grams of acetic acid/square meter of membrane area/h (GMH). This was determined from the slope of the plot of mass of acetate transported from the D-stream into the C-stream vs time, divided by the membrane area.
2. Volume flux. This was measured as the slope of a plot of bulk volume (in liters) vs time, and divided by the membrane area, to give units of L/square meter/h (LMH).
3. Water flux. Because the above volume flux accounts for the transport of both acetate and water, the water flux was obtained by subtracting the mass of acetate from the total mass transported and converting it into volume units with density values obtained from standard tables *(13)*. From a plot of volume of water vs time, the slope was divided by the membrane area to give water flux in units of L/square meter/h (LMH).
4. Energy consumption was measured by recording the voltage of the stack with respect to time at a fixed current density. The area under the curve was integrated using Mathematica 2.2 (Wolfram Research Inc., Champaign, IL) to give energy in units of volts-minutes. This was then multiplied by the current to give watt-minutes, and converted into units of kilowatt-hours (kWh). It was then divided by the mass of acetate transported from the D-stream into the C-stream to yield energy consumption in kWh/kg acetate.

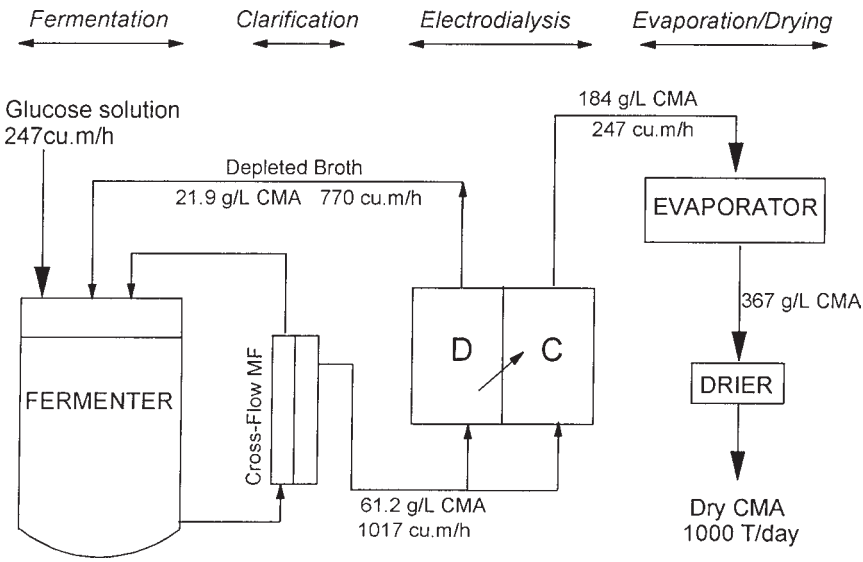

Fig. 1. Manufacture of CMA by fermentation and electrodialysis. Data are for a 1000 ton/d plant. Numbers are volumetric flow rate (m^3/h) and concentration of CMA (g/L).

Results and Discussion

Process Design

A diagram of a possible CMA process with membranes is shown in Fig. 1. The downstream portion is designed in three stages: clarification, electrodialysis for purification and concentration, and final moisture removal by evaporation/drying. The whole fermentation broth is pumped to a microfiltration unit that serves two purposes: to clarify the broth prior to ED and to recycle cells to the fermenter to improve productivity *(5,6)*. The clarified broth is then sent to the ED system. The C-stream, containing the partially purified and concentrated CMA, is sent for evaporation and drying, while the depleted D-stream, containing residual acetate and unutilized nutrients and glucose, is recycled to the fermenter or to the first stage of a multi-stage ED system. Cost estimates presented in this paper are for the MF, ED, and evaporation systems.

Model Acetate Solutions

Figure 2 shows typical trends observed during ED of a model sodium acetate solution at pH 6.8. Acetate was transported from the feed stream (D-stream) into the product stream (C-stream), resulting in an increase in acetate concentration in the C-stream and a decrease in D-stream concentration (Fig. 2A). The bulk volume of each stream changed owing to water transport by electro-osmosis (Fig. 2B). Voltage changes (not shown here; *see 12,14*) also occurred owing to depletion of ions in the D-stream.

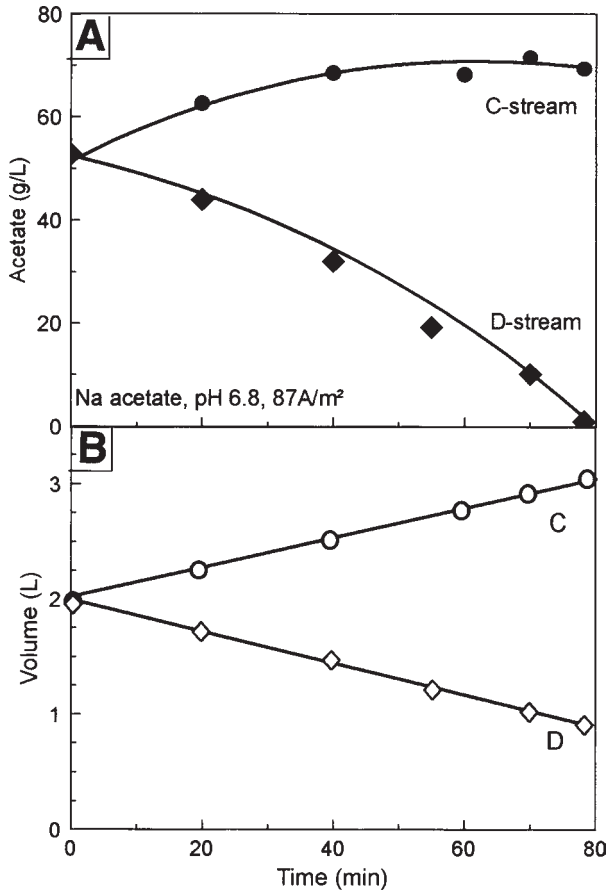

Fig. 2. Typical trends observed in the electrodialysis of model acetic-acid solutions at pH 6.8 and current density of 174 A/m^2. **(A)** Acetic acid concentrations. **(B)** Changes in bulk volume in the C- and D-streams. Initial acetic-acid concentration in each stream was 50 g/L and initial volume in each stream was 2 L. Average of duplicate experiments.

This caused an increase in resistance of the ED stack and an increase in the voltage required to maintain a constant current. ED was halted at a voltage specified by the manufacturer to prevent concentration polarization—which can occur if the concentration in the D-stream becomes too low—as well as to prevent possible membrane damage at the high voltages.

The effects of current density on acetate flux and energy are shown in Fig. 3. Acetate flux increased from 81 GMH at 43 A/m^2 to 399 GMH at 174 A/m^2 while water flux increased from 0.8–2.6 LMH under the same conditions. Unit energy consumption increases at higher current density. Because the rate of acetate transport was greater that of water, simultaneous separation and concentration of acetic acid is possible with ED. Figure 3 also shows similar ED parameters for the model CMA solution at pH 6.8 and for the CMA fermentation broth. The major difference is that CMA

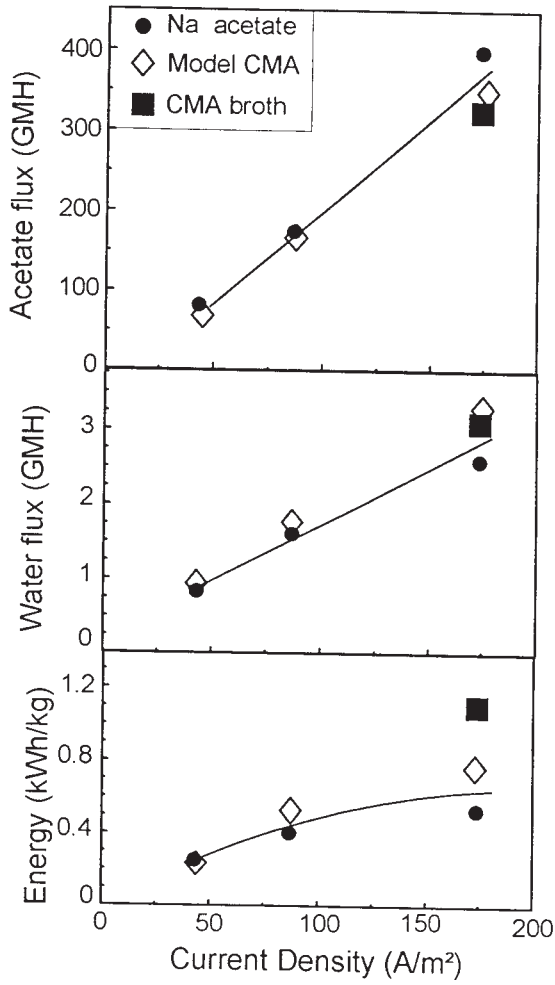

Fig. 3. Effect of current density on ED parameters. Closed circles are for the model sodium acetate solution at pH 6.8. Open points are for CMA model solution at pH 6.8. Closed squares are fermentation broth, pH 6.0.

feed solutions contain divalent cations (Ca^{2+} and Mg^{2+}), which have lower mobility and transport rate than monovalent ions. Thus the acetate flux is slightly lower and the energy consumption is higher. Similar phenomena were observed with lactate solutions *(15)*; the rate of transport of calcium lactate was about half the rate of sodium lactate. Perez et al. *(16)* also observed that the rate of Na^{+} removal was greater than the Ca^{++} removal rate.

Higher initial feed concentration increased acetate flux, decreased water flux, and lowered energy consumption (not shown here: *see* ref. *14*). Increasing pH generally decreased acetate flux slightly *(14)*, perhaps owing to the lower mobility of the cations (Na^{+}, Ca^{2+}, Mg^{2+}) compared to the protonated form of acetic acid. Higher pH also decreased unit energy consumption owing to the higher conductivity of the dissociated salts.

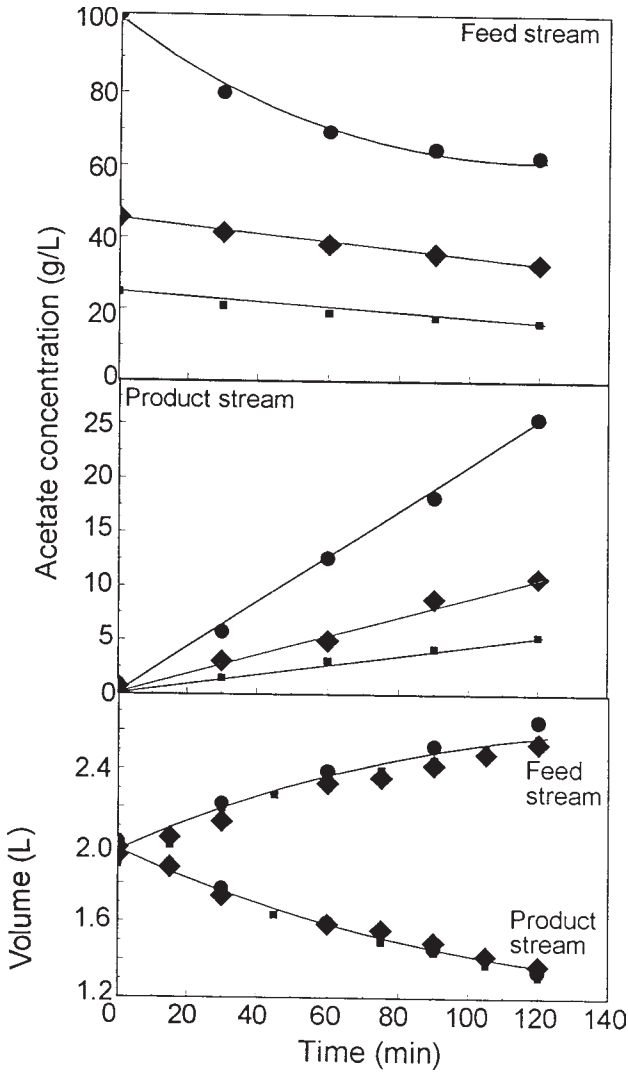

Fig. 4. Diffusion of acetate and osmosis of water during ED. A model solution of sodium acetate at pH 6.8 was recirculated through the feed compartment. Water was recirculated in the product compartment. No current was applied.

Acetate transport also occurred by diffusion since the pore size of ED membranes is equivalent to about 300 mol wt. This can be measured by pumping an acetate solution through the feed compartment and pure water in the product compartment at equal pressure drops, without applying any current. As shown in Fig. 4, transport of acetate occurs from the feed stream to the product stream owing to diffusion. The rate of diffusion depends on the concentration of acetate and pH, as shown in Fig. 5. Thus, mass transfer owing to concentration differences augments the electro-osmotic transport of acetate in the initial stages of ED processing. However, in the later stages,

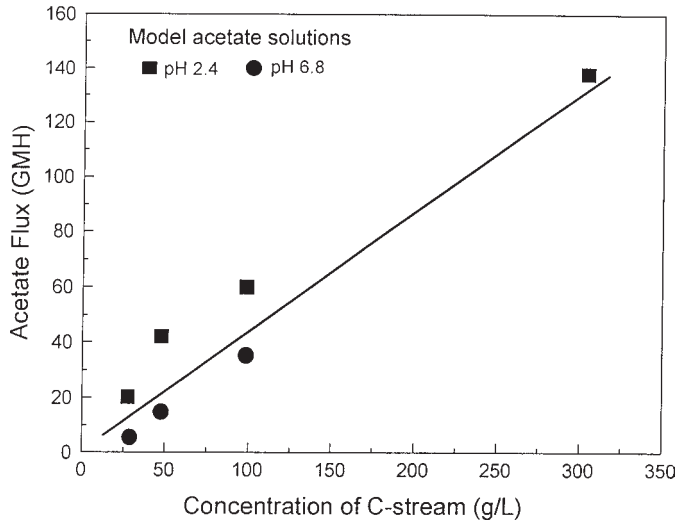

Fig. 5. Effect of acetate concentration (g/L) on diffusion rate (g of acetic acid/m^2/h, GMH).

when the acetate concentration is higher in the product stream, back-diffusion of acetate occurs, which will eventually limit the maximum concentration of acetate possible in the product stream.

There is also a simultaneous transport of water owing to osmosis. Initially, the concentration (and thus the chemical potential) of water is higher in the product stream than in the feed stream. This causes the osmotic transport of water to occur from the product to the feed stream (i.e., in the opposite direction of the acetate). This is also shown in Fig. 5. However, with the application of a current, the rate of co-transport of water (with the acetate ions) is greater than its back-transport due to osmosis, resulting in a net transport of water into the product stream as shown in Fig. 2.

Diffusion also plays a role in transport of sugars and other small uncharged components of the feed stream. This was studied with the model CMA solution, which contained 5 g/L glucose. Glucose flux was 3–7.5 GMH *(14)*, which is much lower than the acetate flux which was 80–400 GMH.

CMA Fermentation Broth

The optimum process should result in maximum concentration of acetate in the product stream with maximum acetate flux and minimum water flux and energy consumption. Multiple-stage electrodialysis (MSED) can be used simultaneously to concentrate and clarify the CMA fermentation broth. Several ED stacks of membranes are placed in series, with each stack operated in a batch-recycle mode or in a continuous feed-and-bleed mode. The required number of stages will be determined by the final concentration of acetate required and the current in each stage. Furthermore, unequal volumes (in the batch recycle mode) or different

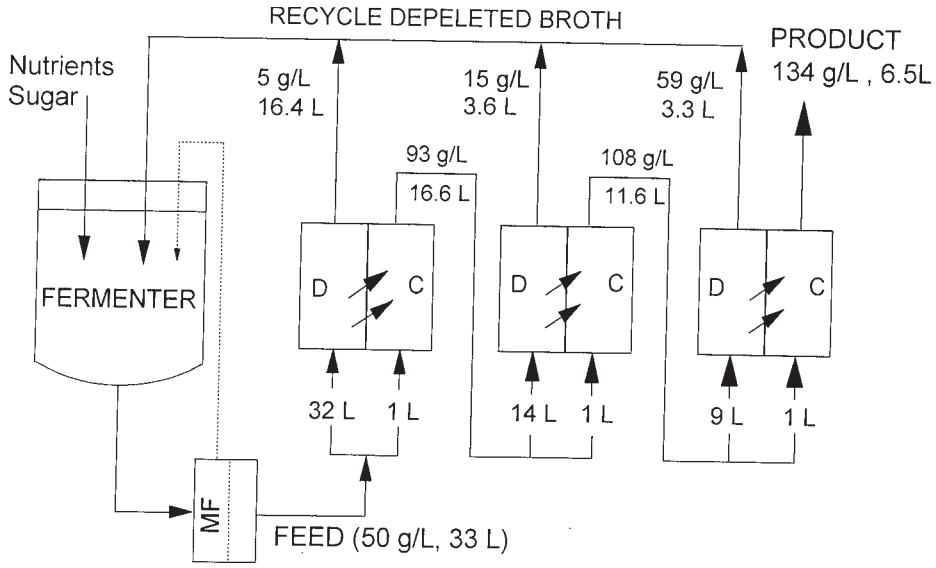

Fig. 6. Multiple-stage electrodialysis (MSED) of CMA fermentation broth. Data refer to volume in liters and concentration of acetic acid (g/L).

flow rates of C- and D-streams (in the continuous mode) could be used to enhance the concentration of acetate. This concept has been demonstrated with vinegar *(12)*.

A schematic diagram of MSED for CMA is shown in Fig. 6. Each stage was operated in the batch-recycle mode. The initial feed volume in the first stage was 32 L of CMA broth in the D-stream, and 1 L of broth in the C-stream. A current density of 174 A/m^2 was applied. Figure 7 shows changes in the acetate concentration during ED in the first stage. The D-stream concentration showed a steady decrease from 49 g/L acetic acid to 5 g/L. Acetate concentration increased in the C-stream to reach an asymptotic value of 93 g/L. The asymptote is owing to a combination of back-transport of acetate from the C-stream into the D-stream at higher concentrations (due to diffusion) and water transport into the C-stream. Also shown in Fig. 7 are volume changes and concentrations of calcium and magnesium in the C- and D-streams of the first stage. Calcium increased from 10.2–18.3 g/L and magnesium increased from 6.6–11.2 g/L.

Data were similar in the 2nd and 3rd stages *(14)*. It should be noted that the feed volume into each succeeding stage was lower than the previous stage because we deliberately chose to start with substantially different volumes in the C- and D-stream compartments (some of the product stream from the previous stage was also used to pre-equilibrate the ED stack, as described in the Materials and Methods section). The final values of acetate concentration and volumes are shown in Fig. 8. There was a slight increase in acetate flux (Fig. 8A), a slight decrease in water flux (Fig. 8A), and a decrease in flux of the cations (Fig. 8C) in succeeding stages. Unit energy

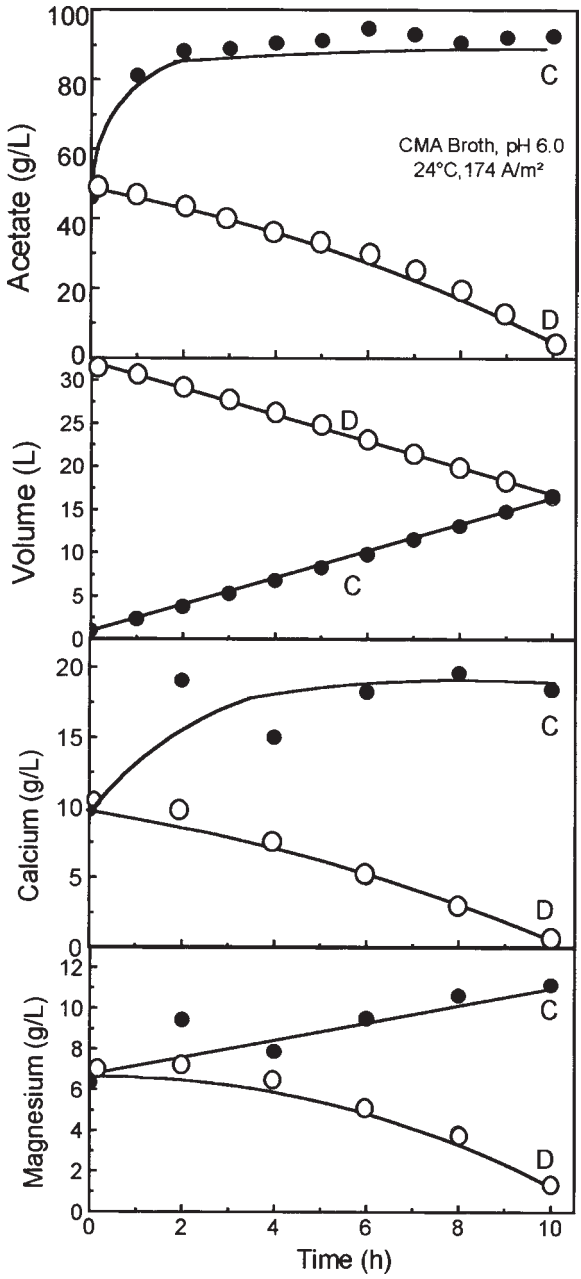

Fig. 7. Volume changes and concentrations of acetic acid and divalent cations in the first stage of MSED of CMA broth. The current density was 174 A/m^2.

consumption decreased in the later stages, probably because concentrations were higher, thus decreasing the resistance of the ED stack.

Although these values for the fermentation broth were comparable to the high-pH model solutions (Fig. 3) the acetate flux was much lower than low-pH acetate feeds such as vinegar, which reached 800 GMH in the 3rd

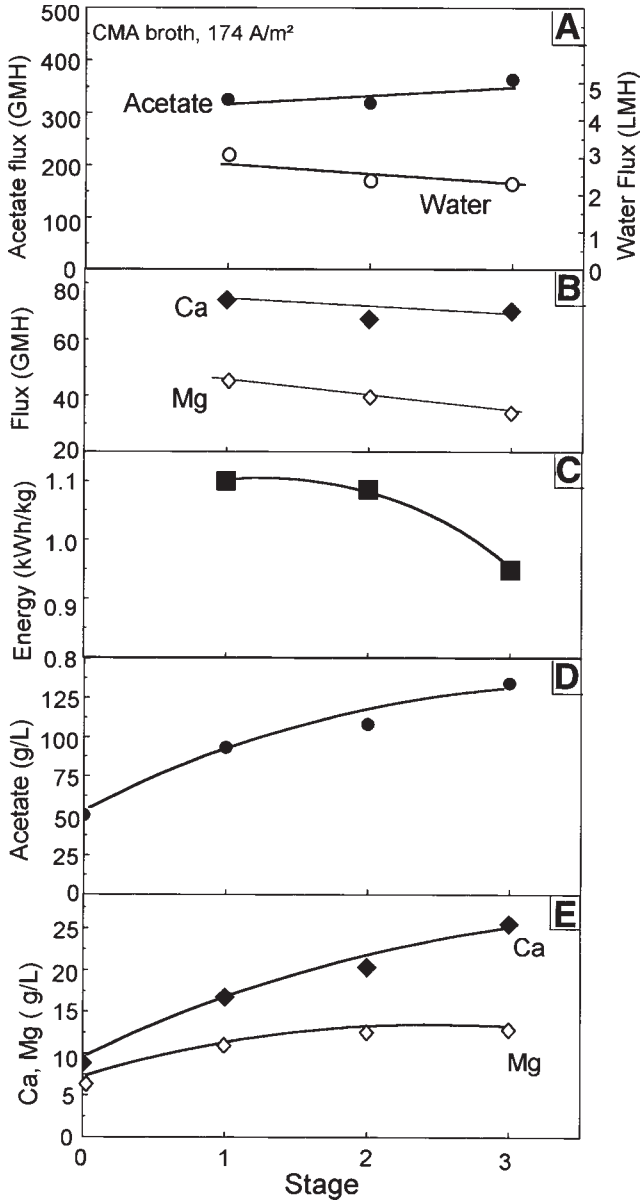

Fig. 8. ED parameters during MSED of CMA fermentation broth as shown in Figs. 6 and 7. Stage "0" is the feed to the MSED system (the microfiltered fermentation broth). Data at the other stages represent outlet conditions.

stage *(12)*. Water flux and energy consumption were 50% lower with the low-pH feeds. In addition, as shown in Fig. 8D, the third-stage product stream had an acetic acid concentration of 134 g/L (178 g/L of CMA), whereas the 3rd stage with vinegar had a concentration of 300 g/L acetic acid *(12)*. The lower performance with high-pH broths such as CMA is owing to the presence of divalent cations, as explained earlier.

A material balance around all the stages indicated acetate recoveries of more than 90% in the C-stream in each stage. The acetate not recovered is in the D-stream, which is recycled back to the fermenter or to the first stage of the ED stack. Higher current densities could have increased flux and the recovery. Higher recovery could also be achieved by increasing the residence time in the ED stacks. However, owing to back-diffusion of acetate from the product to the feed stream, and the relatively high water-transport rates, the concentration of acetate in the product stream would have declined, as observed with vinegar *(12)*. Thus, more stages with higher current densities should be used rather than prolonging the ED.

It was also observed that the electrode stream (consisting of 0.2 *N* sodium sulfate at pH 2.0) became cloudy when processing CMA feeds. Analysis of the electrode stream showed significant levels of calcium and magnesium, probably owing to migration from the feed streams. These ions would react with the sulfate ion to form insoluble calcium and magnesium sulfates. These could also be responsible for increasing the resistance of the stack, resulting in higher energy consumption with the CMA broth (Fig. 3). Yao and Toda *(16)* also observed a white colloidal precipitate during ED of calcium lactate, which they surmised could have lowered the rate of demineralization.

The concentrated CMA solution from the ED system was clear with no trace of suspended particles and substantially decolored. Fouling of the ED stack was monitored by comparing the flux of a model acetic acid solution (55 g/L, pH 2.4) before and after MSED experiments. There were no changes in ED performance, indicating no permanent fouling of the membrane.

Economics

A preliminary estimate of the cost of ED of the CMA broth is shown in Tables 1–3. This was based on a production of 1000 tons/d of dried CMA, as shown in Fig. 1. This required a feed flow rate of 1017 m^3/h of microfiltered broth containing 50 g/L acetic acid (equivalent to 61.2 g/L CMA) into the D-stream of the MSED system. Acetate will be concentrated by passage through three ED stacks until a final concentration of 150 g/L acetic acid (183.8 g/L CMA) is obtained. It was assumed that a feed-and-bleed mode was used at a current density of 350 A/m^2 (typical for industrial units). The membrane unit would be operated for 22 h/d with 2 h for cleaning. The output from the ED system would be 247 m^3/h containing 184 g/L CMA (150 g/L acetic acid). The depleted D-stream would be 770 m^3/h containing 21.9 g/L CMA. Process engineering parameters (acetate flux, water flux, and energy consumption) were calculated from data presented earlier. A six-effect evaporator (for final concentration to 300 g/L acetic acid) is shown in the diagram and has been included in the design, but the drier has not been included.

For comparison of costs, two options have been considered. Option 1 is direct evaporation of the MF-clarified broth from 50 g/L acetic acid to 300 g/L using a six-effect evaporator. Option 2 is a process in which the

Table 1
Process and Equipment Specifications for Downstream Processing of CMA Fermentation Broths (Basis: 320,000 Tons/Yr of Dry CMA)

Equipment	Option 1	Option 2
MF (Clarification with ceramic membranes)		
Broth flow rate (L/h)	1,017,992	1,017,992
Flux (LMH)[a]	300	300
Membrane area (m^2)	3,393	3,393
Energy consumption (kW)[b]	867	867
ED (Concentration and purification)		
Acetate flux (GMH)[c]	—	706
Membrane area (m^2)	—	175,866
Energy consumption (kW)[c]	—	196,922
Evaporation		
Water evaporated (L/h)	848,325	123,866
Steam usage (kg/h)[d]	163,454	23,866
Energy consumption (kW)[a]	2,430	355

[a]Han and Cheryan *(9)*.
[b]Cheryan *(4)*.
[c]Extrapolated from Figs. 3 and 8.
[d]Steam economy = 5.2 kg water evaporated/kg steam *(13)*.

Table 2
Capital Investment ($) for the Downstream Processing of Acetate Fermentation Broths

Item	Option 1	Option 2
Membranes		
MF (Ceramic)[a]	7.3 million	7.3 million
ED[b]	—	87.5 million
Evaporator[c]	5.7 million	2.0 million
Fixed capital		
Total	13.0 million	96.8 million
$/ton/yr capacity	40.0	302.0

[a]Cost basis of $2150/$m^2$ *(4,9)*.
[b]$500/$m^2$ (personal communication from membrane manufacturers).
[c]For 6-effect evaporator *(9)*.

MF clarified broth is concentrated to 150 g/L by ED and evaporated to 300 g/L. Table 1 shows the specifications of the equipment. The capacity of each membrane unit is in square meters of membrane area, whereas the evaporator has been estimated on the basis of the water evaporation rate needed for a particular option.

The fixed capital costs are tabulated in Table 2. The capital cost for the MF+ED+evaporation process (Option 2) is $302/ton/yr of CMA, whereas the operating cost (Table 3) is $295/ton/yr. A 50% credit for the nutrients

Table 3
Annual Operating Cost ($/Yr) for Downstream Processing

Item	Option 1	Option 2
Electric power for membranes ($0.05/kwh)		
MF	305,400	305,400
ED	—	69,300,000
Energy for evaporation	8,550,000	125,000
Membrane replacement[a]		
MF[a]	271,400	271,440
ED[b]	—	17,586,000
Membrane cleaning ($18/m^2/yr)	61,100	3,290,000
Labor ($24/h)	15,000	30,000
Maintenance (3% of fixed capital)	390,000	2,904,000
Depreciation (10% of fixed capital)	1,300,000	9,680,000
Total cost	10,892,900	103,497,800
Nutrient credit[c]	—	(8,960,000)
Net downstream cost		
$/yr	10,892,900	94,537,800
$/ton of acetate	34	295

[a]Five-yr life for ceramic membranes: $80/m^2/yr. See *(4)* for calculations.
[b]One-yr life for ED membranes at $100/m^2/yr.
[c]Assuming 50% recycle of nutrients, based on data of Witjitra et al. *(3)*.

recycling stream has been incorporated into the calculations based on prior work *(3)*. Although there is substantial savings in evaporation costs in Option 2, the costs of membrane replacement, cleaning, and electric power consumption for ED concentration more than offsets this benefit. In contrast, the cost of MF+ED processing of vinegar is $135/ton of acetic acid *(14)*.

In summary, the high operating and capital expense for electrodialysis may be justified if the product (acetate) needs to be partially purified and concentrated, e.g., for sodium and potassium acetates. In the case of CMA, it is used primarily as a road de-icer and a substantial purification is not necessary. In that case, Option 1 is preferred: capital costs are only $40/ton/yr and operating costs are $34/ton of CMA.

Acknowledgments

Funds were provided by the Illinois Corn Marketing Board, Minnesota Corn Promotion and Research Council, U.S. Department of Agriculture through the NRICGP program (#92-37500-8014), U.S.D.A. National Needs Fellowship program, and the Illinois Agricultural Experiment Station.

References

1. Parekh, S. R. and Cheryan, M. (1991), *Appl. Microbiol. Biotechnol.* **36,** 384–387.
2. Parekh, S. R. and Cheryan, M. (1994), *Biotechnol. Lett.* **16,** 139–142.
3. Witjitra, K., Shah, M. M., and Cheryan, M. (1996), *Enzyme Microbial Technol.* **19,** 322–327.

4. Cheryan, M. (1998), *Ultrafiltration and Microfiltration Handbook*, Technomic, Lancaster, PA.
5. Parekh, S. R. and Cheryan, M. (1994), *Enzyme Microbial Technol.* **16,** 104–109.
6. Shah, M. M. and Cheryan, M. (1995), *Appl. Biochem. Biotechnol.* **51–52,** 413–422.
7. Han, I. S. and Cheryan, M. (1995), *J. Membrane Sci.* **107,** 107–113.
8. Raman, L. P., Rajagopalan, N., and Cheryan, M. (1994), *Chem. Eng. Progr.* **90(3),** 68–74.
9. Han, I. S. and Cheryan, M. (1996), *Appl. Biochem. Biotechnol.* **57/58,** 19–27.
10. Yen, Y. H. and Cheryan, M. (1991), *Trans. Inst. Chemical Engrs. (UK).* **69(Part C),** 200–205.
11. Yen, Y. H. and Cheryan, M. (1993), *J. Food Eng.* **20,** 267–282.
12. Chukwu, U. N. and Cheryan, M. (1996), *J. Food Sci.* **61,** 1223–1226.
13. Perry, R. H., Green, D. W., and Maloney, J. O. (1984), *Perry's Chemical Engineering Handbook,* 6th ed. McGraw-Hill, New York.
14. Chukwu, U. N. (1995), Ph. D. thesis, University of Illinois at Urbana-Champaign, Urbana, IL.
15. Yao, P. X. and Toda, K. (1990), *J. Gen. Appl. Microbiol.* **36,** 111–125.
16. Perez, A., Andres, L. J., Alvarez, R., Coca, J., and Hill, C. G., Jr. (1993). *J. Food Process Eng.* **17,** 177–190.