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Downstream Processing of Acetate Fermentation Broths by Nanofiltration

IN SOO HAN AND MUNIR CHERYAN*

University of Illinois, Agricultural Bioprocess Laboratory, 1302 West Pennsylvania Avenue, Urbana, IL 61801

ABSTRACT

Acetate can be separated from fermentation broths and partially purified by nanofiltration (NF). Membrane performance was a function of pressure, pH, concentration of acetate, temperature, and the presence of other media components. With Nitto-Denko's NTR729 membrane, average acetate rejection was 60%, glucose rejection was 99%, and flux was 15 L/m²/h at 200 psig, 30°C, pH 5.6, and 20 g/L acetic acid. The best downstream strategy is to clarify the fermentation broth by microfiltration (MF), recycle the cells for improving fermenter productivity, nanofilter the cell-free broth, and then evaporate the permeate. The cost of ceramic MF and NF purification is about $66/t acetate, compared to the cost of potassium acetate ($950/t) or calcium-magnesium acetate ($700/t).

Index Entries: Acetate; membrane technology; nanofiltration; separation.

INTRODUCTION

Acetic acid is one of the most important commodity chemicals, with a US production of 3.6 billion lb/yr, representing a market value of $1.1 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 the anaerobic fermentation of dextrose by *Clostridium thermoaceticum*. This organism, however, produces acetate at low concentrations (2–5%) and over long periods (3–5 d), unless the medium is supplemented with expensive nutrients *(1–3)*.

The feedstock (e.g., dextrose) and downstream processing constitute the largest costs in the manufacture of acetates. Membrane technology can be used in most phases of downstream processing. Microfiltration (MF) and ultrafiltration (UF) are effective for separation and recycling of the cells *(4–6)*. Nanofiltration (NF) is a relatively new membrane technique that can separate organic acids (depending on the degree of dissociation) and monovalent salts from sugars and other organic compounds *(7,8)*. NF should allow us to purify the acetate and recycle the nutrients simultaneously, thus lowering the cost of production. Furthermore, a combination of high-rejection (HR) and low-rejection (LR) membranes could be used to obtain

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

very high concentrations of acetic acid. This article reports on the potential applicability of membrane technology for the separation, purification, and concentration of acetates from fermentation broths. Membrane performance data obtained with a CMA fermentation broth were combined with earlier studies on model sodium acetate solutions to obtain a preliminary cost estimate of applying membrane technology in downstream processing.

MATERIALS AND METHODS

Flux and rejection characteristics of several membranes were studied using a stirred filtration cell as described earlier *(7)*. The fermentation broth was from our CMA fermentation studies in which dextrose was fermented in the presence of yeast extract and other trace elements by *C. thermoaceticum (5,6)*. Dolime (CaO·MgO) was used as the neutralizing agent during the fermentation. Prior to use in the NF test cell, the broth was clarified using a 0.2-μ ceramic MF module (CeraMem Separations, Waltham, MA) and its pH adjusted using pure glacial acetic acid, if necessary.

Several reverse osmosis (RO) and NF membranes were evaluated with model acetate solutions. From this study *(7)*, two membranes were selected for the first NF-purification stage: NTR729 (Nitto-Denko, Japan) and MX07 (Osmonics, Minnetonka, MN). Rejection (R) of components is calculated as:

$$R = 1 - C_p/C_R \quad (1)$$

where C_p is concentration of a component in the permeate and C_R is concentration of the component in the retentate. Flux data can be correlated by the following equation:

$$J = A\,(P_T - \Delta\pi) \quad (2)$$

where J is flux (LMH), P_T is the applied pressure, $\Delta\pi$ is the osmotic pressure difference across the membrane, and *A* is a membrane permeability coefficient.

Acetate and glucose were analyzed by high-performance liquid chromatography (HPLC) using the HPX-87 column (Bio-Rad, Hercules, CA) as described earlier *(5–7)*. Unless otherwise mentioned, the concentration of acetates is reported in terms of acetic acid. An acetic acid concentration of 1 g/L is equivalent to 1.225 g of CMA and 1.375 g 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.

RESULTS AND DISCUSSION

Process Design

A diagram of a possible downstream process with membranes is shown in Fig. 1. The process is designed in three stages: clarification, purification, and concentration. After the fermentation, the whole fermentation broth is pumped to a microfiltration unit that serves two purposes: to clarify the broth prior to NF and to recycle cells to the fermenter to improve productivity *(5,6)*. The clarified broth is then sent to the first of two NF stages. The first is for separation/purification of the acetate; it consists of membranes with low acetate rejection and high glucose rejection (glucose was used as an index of nutrients). Since the acetate passage was significantly better at low pH *(7)*, the fermentation broth was adjusted to pH 5.6. This pH

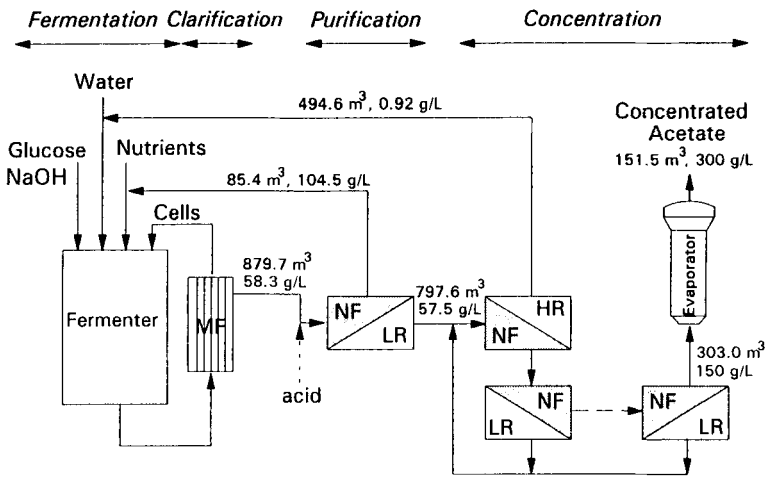

Fig. 1. Process for downstream processing of acetate fermentation broths. Data refer to volumetric flow rate (m^3/h) and concentration of sodium acetate (g/L).

value was a compromise based on the rejections of acetate vs glucose, and the cost of acidifying the broth. This required 3.8 L of full-strength glacial acetic acid/m^3 of sodium acetate fermentation broth, based on titration curves.

The retentate from the NF-purification stage contains the nutrients and some acetate, which are recycled to the fermenter. The permeate from this stage is a dilute and substantially purified acetate solution. This permeate stream is sent to the second NF operation, a series of HR and LR membranes. The HR membrane (e.g., FT-30, Dow, Midland, MI or TLC, Fluid Systems, San Diego, CA) should produce a permeate that is mostly water, which can be recycled to the fermenter. The retentate, containing partially concentrated acetate, is sent to an LR membrane (e.g., NF40, Dow). Owing to the partial passage of acetate through the LR membrane, the $\Delta\pi$ will be low, thus keeping the driving force (and flux) at reasonably high levels, according to Eq. (2). The retentate from this LR membrane, containing higher acetate concentration than the feed and the permeate (since it is partially rejected), is sent to more LR units until the desired concentration of acetate is obtained. The permeate from these particular LR modules contains dilute acetate, which can be recycled back to the first HR membrane in this stage. Thus, in the ideal case, the product from this series of HR–LR membranes is water (from the HR membrane) and concentrated acetate (from the last LR membrane stage).

The six-effect evaporator (for final concentration up to 300 g/L) shown in Fig. 1 has been included in the economics. Depending on the nature of the product, a subsequent drying step may be needed (e.g., for CMA) or further evaporation (e.g., for sodium or potassium acetates). This last moisture removal step has not been included in this analysis.

Membrane Performance

Initial studies were conducted with low-strength CMA fermentation broth, which contained 17 g/L acetic acid (20.8 g/L CMA). When adjusted from pH 6.8 to 5.6 with concentrated acetic acid, the acetic acid concentration of the tested sample

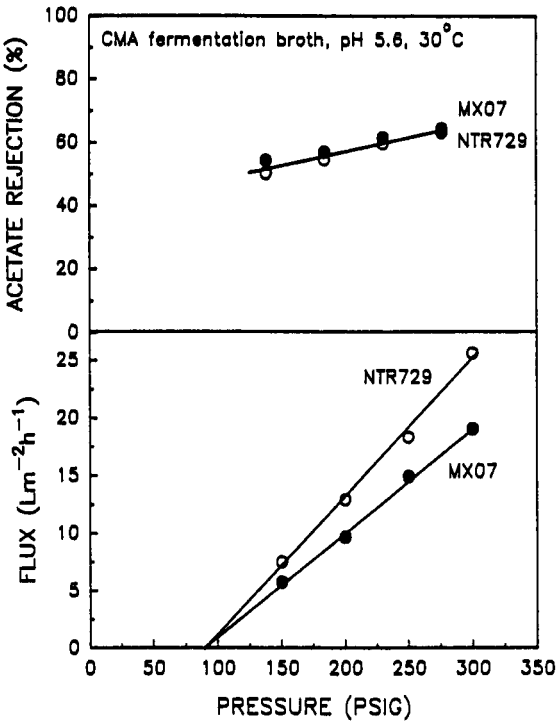

Fig. 2. Performance of NF membranes with CMA fermentation broth. The pH of the CMA broth was adjusted from 6.8 to 5.6, resulting in a final concentration of 19 g/L acetic acid.

increased to 19 g/L. Other components included about 26 g/L other total solids, mostly salts and vitamins (the Na^+ and K^+ ions are in the culture medium). As shown in Fig. 2, flux was 10–15 L/m²/h (LMH) at 200 psi, whereas the rejection was 60%. In contrast, model sodium acetate solution had a flux of 45 LMH and 40% rejection under the same conditions with the same membranes *(7)*. The different ionic conditions were probably responsible for the deviation from model solution behavior. For example, the observed osmotic pressure difference ($\Delta\pi$) was about 90 psi, and permeability constant (A) was 1.81 LMH/bar for the NTR729 membrane at 30°C. In contrast, with model solutions at 20 g/L, $\Delta\pi$ was 60 psi and A = 4.03 LMH/bar. The higher osmotic pressure of the fermentation broth was owing to other salts and vitamins in the culture medium.

The behavior of the minerals (K^+, Na^+, Ca^{2+}, Mg^{2+}) during NF of CMA fermentation broth is shown in Fig. 3 with the NTR729 membrane (this was a different batch of CMA broth: This tested sample contained 23 g/L acetate). The concentration of the elements in the retentate did not change much as the pressure was increased. However, higher pressure caused a higher volumetric flux, which resulted in a dilution of the components in the permeate, as shown in the upper graph of Fig. 3. This is the main reason for the observed phenomenon of higher apparent rejection at higher pressures.

In addition, as expected of NF membranes *(8)*, rejections of Ca^{2+} and Mg^{2+} were higher than Na^+ and K^+ rejections. Although the Na^+ and K^+ concentrations were about the same in the retentate and permeate, indicating low rejection of these ions,

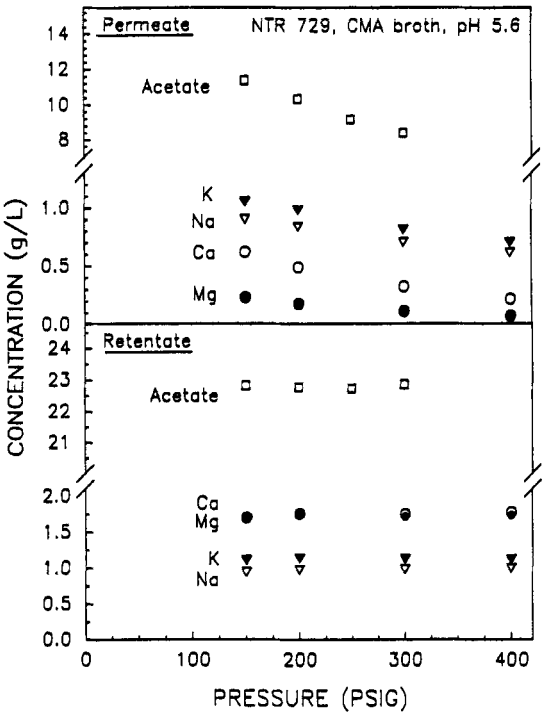

Fig. 3. Mineral composition of permeate and retentate from the NF of CMA fermentation broth. The pH of the CMA broth was adjusted from 6.8 to 5.6, resulting in a final concentration of 23 g/L acetic acid.

the permeate contained much lower levels of Ca^{2+} and Mg^{2+} than the retentate. At 200 psi, rejections of Na^+ and K^+ were 14%, whereas Ca^{2+} rejection was 72% and Mg^{2+} was 90%. At pH 5.6, acetic acid was 87% ionized (*7*), and its separation was dependent on the cation composition of the feed. Thus, the nature of the cations and the pH influence the degree of separation of organic acids.

Figure 4 shows a batch concentration with the NTR729 membrane. Glucose was added to the CMA broth to 10 g/L and acetic acid was 20 g/L. The concentration of acetic acid and glucose is plotted against the volume concentration ratio (VCR) for both permeate and retentate. As the concentration of acetate increases in the feed/retentate, the concentration of acetate in the permeate increases. Until a VCR of ~3 (corresponding to 40 g/L of acetate and 30 g/L of glucose), rejections were constant at ~95 and 55%, respectively. Above VCR 3, the rejections decreased for both compounds, indicating perhaps that the ion-exchange capacity of the membrane had been exceeded. Similar effects (higher acetate concentration causing a decrease in acetate rejection) were reported for model systems (*7*).

The product (permeate) from the NTR729 membrane was clear and colorless, in contrast to the dark-colored feed and retentate. The HPLC chromatograms also showed a substantial degree of purification (*9*).

Economics

The basis for the economic analysis is a 1000 t/d sodium acetate plant. The cost estimates presented in this article are for downstream processing from the MF to

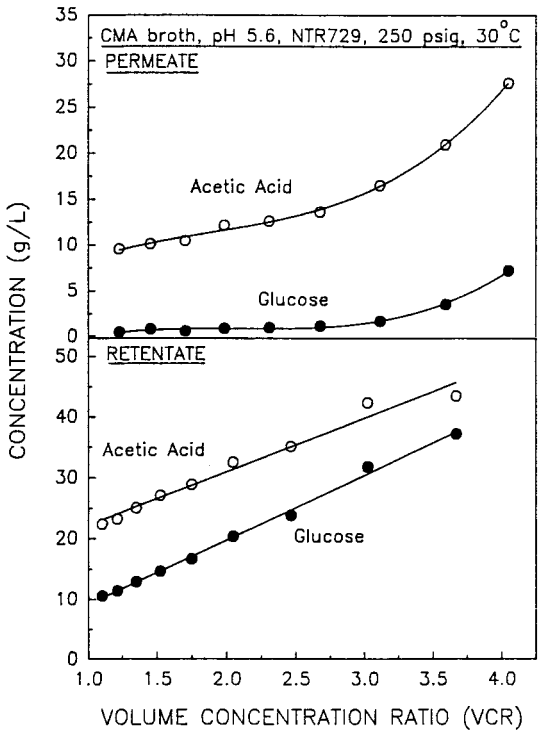

Fig. 4. Effect of concentrating CMA fermentation broth with NTR729 membrane on retentate and permeate concentrations. The pH of the CMA broth was adjusted from 6.8 to 5.6, resulting in a final concentration of 20 g/L acetic acid. Glucose (10 g/L) was added to the broth.

the evaporation step as shown in Fig. 1. The target concentration of the product from the evaporator is 300 g/L. For comparison purposes, three options have been considered: a process as shown in Fig. 1 (labeled "Option 1—MF, NF, NF"), a process where there is no NF concentration ("Option 2—MF, NF") and a process that bypasses both NF-concentration and NF-purification stages, so that the MF-clarified broth goes directly to the evaporator (labeled "Option 3—MF"). The membrane units are operated for 22 h/d, with 2 h for cleaning. Broth from the fermenter is at 60°C, acetic acid concentration of 58.3 g/L, and pH of 6.8.

MF

Two types of MF membrane modules were considered: hollow fibers of 2–3 mm internal diameter (available from Koch-Romicon, A/G Technology, or Dow), and ceramic (alumina) membrane modules (e.g., with 3–4 mm internal diameter from US Filter, Warrendale, PA or with 2-mm channel height from CeraMem). The broth flow rate from the MF system is 879,737 L/h, based on a material balance as shown in Fig. 1. From performance studies done in our laboratory and the relative capital and replacement costs for these membrane modules, the CeraMem ceramic membrane system was chosen (*see* Table 1 for operating parameters, concentrations, flows, and unit costs).

Table 1
Specifications and Operating Levels of Membrane Processes
Used for Downstream Processing of Acetate Fermentation Broths

Operating parameter	MF	NF purification	NF concentration
Module type	Ceramic	Spiral[a]	Spiral[a]
Operating pressure (psi)	75	500	700
Temperature (°C)	60	50	50
pH	6.8	5.6	5.6
Pressure drop/module (psi)	20	15	15
Recirculation (GPM/module)	300	200	200
Energy (W/m^2)	250	55	55
Membrane area (m^2)	2513	20,712	201,338
System cost ($/$m^2$)	2150	225	225
Membrane replacement cost ($/$m^2$/yr)[b]	80	50	50
Feed flow rate (m^3/h)	—	883.1	797.6
Permeate flow rate (m^3/h)	879.7	797.6	494.6
Acetate in feed (g/L)	58.3	62.1	57.5
Acetate in retentate (g/L)	58.3	104.5	150
Acetate in permeate (g/L)	58.3	57.5	0.92

[a]8 × 40 in. modules, with 60-mil spacers, 25 m^2 each.
[b]Five-year life for ceramic membranes, 1-yr life for NF polymeric membranes.

NF Purification

The permeate from the MF unit is the feed to the NF-purification step. The operating parameters and flows for this step are given in Table 2. The NF area is determined as follows:

$$\text{NF membrane area } (m^2) = \text{NF permeate flow (L/h)/NF flux (LMH)} \quad (3)$$

Because the concentration of acetate and glucose is continuously increasing during a batch process or with each stage in a feed-and-bleed process *(4)*, there is a simultaneous increase in osmotic pressure, which causes flux to decrease and eventually become zero when the osmotic pressure of the retentate is the same as the applied transmembrane pressure. To design this stage, a computer program was written to take flux and rejection data from our previous work *(7,9)* and perform calculations until the final product stream met the requirements for the process: In this case, it is a product stream (permeate) concentration of 57.5 g/L acetate at a total permeate flow rate of 797,617 L/h (these parameters come from the design of the NF-concentration stage: *see next section*). The outer loop varied the amount of area to meet the requirements.

A batch process cannot achieve 100% recovery of the acetate owing to the buildup of the osmotic pressure. Some acetate remains in the retentate and will have to be recycled back to the fermenter with the other nutrients. A high recovery of acetate (i.e., a high VCR) in the purification stage is desirable, because less acetate recovery in this step means a higher feed rate into the NF unit, which then increases the MF membrane area. At maximum VCR, recovery of acetate is maximized, MF

Table 2
Capital Investment ($) for the Downstream Processing of Acetate Fermentation Broths (Basis: 320,000 t/yr of Acetate Production)

Item	Option 1, MF, NF, NF	Option 2, (MF, NF)	Option 3, (MF)
Membranes			
MF (CeraMem)	4,091,200	4,691,200	4,158,400
NF purification	4,538,900	4,538,900	0
NF concentration	45,319,000	0	0
Installation (10% of 1)	5,454,910	923,010	415,840
Evaporator[a] (installed)	2,199,300	4,850,100	4,850,101
Total fixed capital	62,203,310	15,003,210	9,424,341

[a]From Tejayadi and Cheryan (*10*).

area is minimized, but NF area is maximized. Thus, there is an optimum VCR at which the NF-purification step should be operated to obtain a net minimum cost. For this case, the optimum VCR was 10.31 based on economic analysis (*9*), resulting in a net 82.93% recovery of the acetate, where recovery is defined as follows:

$$\text{Acetate recovery (\%)} = [\text{acetate (kg) from last stage of NF concentration/ acetate (kg) in the feed to the NF-purification stage}] \times 100 \quad (4)$$

The average NF flux was 39.5 LMH, resulting in an NF-purification area of 20,172 m^2, and an MF area of 2513 m^2. Table 1 shows flow rates and acetate concentrations in this step.

CONCENTRATION BY NF

The criteria in this step are:

1. The acetate concentration in the retentate of the final stage should be 150 g/L;
2. The permeate from the first stage in this step should be as close to zero acetate as possible; and
3. The weight of acetate produced should be 1000 t/d, which translates into an output of 303,030 L/h of product stream containing 150 g/L of acetate.

The type of modules used here are essentially the same as for the NF purification step, except for the membrane within the modules. The operating parameters and costs are shown in Table 1.

The first module in this operation is used only for water removal, using an HR membrane. This permeate could be recycled to the fermenter as make-up water. The flux-concentration data for this stage was obtained from our earlier

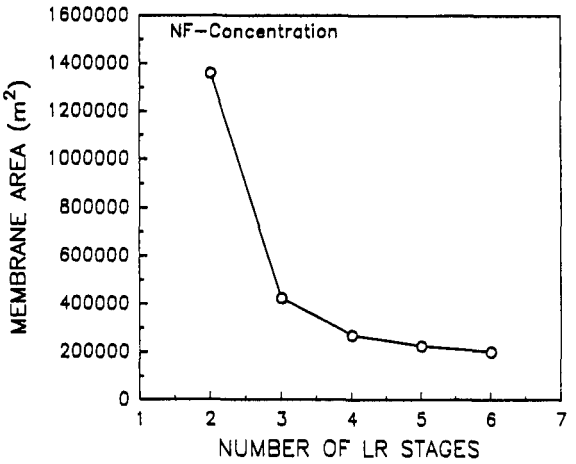

Fig. 5. Effect of number of LR stages in the NF-concentration operation on the membrane area required in the NF-concentration operation.

study *(7,9)*. By increasing the number of LR membranes, higher flux could be achieved in each membrane owing to the smaller concentration gradient. The permeates from LR membranes are recycled back to the feed stream of the first (HR) membrane. By trial and error, the intermediate retentate concentration of each stage was obtained. The effect of number of stages on area is shown in Fig. 5. At a minimum, one HR membrane and two stages of LR membranes are required. A six-stage NF-concentration system was selected as a compromise.

Unit Costs

The most important parameter for determining capital cost is the membrane area in each stage. Table 1 shows some of these unit costs. Table 2 shows fixed capital costs for the process. There is a considerable difference in cost between Option 1 and Option 2, owing to high cost of using NF for concentration to 150 g/L acetate. However, the difference in capital cost between Options 2 and 3 may be justified if (1) there is a need for a purified acetate product or (2) if the recycle of the nutrients can partially offset the cost of NF purification. There are no data available as yet on the feasibility of recycling the spent nutrient broth. Thus, we have assumed only a 50% credit for the nutrients, i.e., a reuse of the nutrients only once or a continuous recycle of the nutrients with a 50% make-up of the nutrients.

Table 3 shows the annual operating cost with the three options. There is a substantial saving in evaporation cost with Option 1, but this is more than offset by the costs of membrane replacement, cleaning, and electric power needed for NF concentration. With Options 2 and 3, the net downstream cost (excluding drying) adds only \$37–66/t of acetate. This is small compared to the cost of CMA (\$700/t) or potassium acetate (\$950/t). A large portion of the operating costs is for purchasing acetic acid to lower the pH of the broth for NF purification. Efforts are under way in our laboratory to adapt the *C. thermoaceticum* culture to operate at lower pH. If successful, this would significantly lower the downstream processing cost.

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

Item	Option 1 (MF,NF,NF)	Option 2 (MF,NF)	Option 3 (MF)
Electric power for membranes			
MF ceramic	258,016	258,016	228,448
NF purification	203,084	203,084	0
NF concentration	2,029,749	0	0
Energy for evaporation	2,413,551	10,165,774	10,165,774
Membrane replacement			
MF ceramic	201,040	201,040	201,040
NF purification	1,008,645	1,008,645	0
NF concentration	10,068,897	0	0
Membrane cleaning ($18/m^2/yr)	4,039,974	415,890	46,782
Labor ($24/h)	30,000	15,000	15,000
Maintenance (3% of fixed capital)	1,866,101	450,096	282,730
Depreciation (10% of fixed capital)	6,220,336	1,500,321	942,434
Acetic acid for pH adjustment ($0.68/L)[a]	16,003,610	16,003,610	0
Total cost	44,343,003	30,221,476	11,882,208
Nutrient credit[b]	(8,960,000)	(8,960,000)	0
Net downstream cost:			
$/yr	35,383,003	21,261,476	11,882,208
$/t of acetate	110.6	66.4	37.1

[a]Anon. *(11)*.
[b]Assuming 50% recycle of nutrients, based on data of Witjitra et al. *(3)*.

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