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Economic Evaluation of a Multicompartment Bioreactor for Ethanol Production Using *In Situ* Extraction of Ethanol

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ABSTRACT

We have previously described a multicompartment reactor that can be used with yeast (*Saccharomyces cerevisiae*) for ethanol production from a starch hydrolysate. By separating a solvent layer (tri-normal-butylphosphate, or TBP) from a cell layer, ethanol was extracted *in situ* and phase toxicity was prevented. Pressure cycling of the gas phase can be used to reduce significantly mass-transfer limitations that often limit entrapped-cell systems. A preliminary economic evaluation shows that with TBP the multicompartment reactor is generally more economically favorable at low volumes, and the traditional system is more favorable at high volumes. Improved solvents can increase economic viability at high volumes (10^8 L/yr of 95% ethanol).

Index Entries: Ethanol production; bioreactors; *in situ* extraction; economic evaluation.

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INTRODUCTION

The economic production of ethanol via fermentation is difficult. The use of immobilized cells, which facilitates continuous operation and maintains high cell density, has been considered an important strategy to improve productivity. However, immobilized cells are limited because of end-product inhibition and CO_2 evolution, which can disrupt the immobilizing matrix in some immobilization methods. Such effects have been particularly evident with membrane-entrapped yeast cultures (*1*).

A major constraint of ethanol fermentation processes is a decrease of the growth of cells and of the specific ethanol production rate (*2,3*) because of the accumulation of end products. To reduce fermentation plant size and minimize separation costs, high sugar concentration in the feed is important, and high sugar concentration can be used only if ethanol inhibition can be circumvented (*4,5*). If ethanol is removed *in situ* from the fermentation broth, then the ethanol concentration in the fermenter can be maintained at such a level that inhibitory effects on growth rate and ethanol fermentation rate are minimized. This scheme will result in lower fermenter volumes at a given ethanol production level. Various methods have been proposed for the simultaneous formation of ethanol and its removal from the broth. Among these are vacuum fermentation (*6*), flash fermentation (*7*), adsorption onto solid, porous adsorbents (*8*), adsorption onto ion-exchange resins (*9*), dialysis fermentation (*10*), and liquid–liquid extractive fermentation (*7,11–14*).

Among these alternatives, the liquid–liquid extraction process has been reported to be the cheapest (*15*). In this process, a solvent is used that can selectively extract the end products from the fermentation broth, preferably with only minute extractions of water and nutrients. Even this process has met with limited success, largely because the choice of solvent has been severely limited by cell toxicity and selectivity for the end products.

Thus, the choice of solvent is critical to the development of an effective liquid–liquid extraction process. Some important criteria for such solvents are

1. High distribution coefficient: The solvent must selectively extract ethanol with minimal extraction of glucose
2. Nontoxicity: The solvent should be biocompatible with the microorganism
3. Separation: The solvent must have a relatively high boiling point for easier separation from product
4. Low distribution coefficient for water: The solvent should be immiscible in the aqueous phase.
5. Commercially availability at relatively low cost
6. The solvent should be noncorrosive
7. Low viscosity
8. Large difference in density from the aqueous phase

Table 1
Examples of Distribution Coefficients For Ethanol With Various Organic Solvents

	Solvent	Distribution Coefficient
Minier and Goma (11)	n-butanol (20C)	3.0
	n-hexanol (28C)	1.0
	heptanol-3 (25C)	0.75
	octanol-2 (28C)	0.8
	dodecanol-1 (30C)	0.35
	heptadecanol (25C)	0.3
Matsumura and Markl (12)	2-ethyl-1-butanol	0.83
	tri-n-butyl phosphate	0.79
	sec-octanol	0.60
	3-phenyl-1-propanol	0.77
	polypropylene glycol P-1200	0.58
Ishii, *et al.* (17)	Freon E	0.20
	octadecafluorodecalin	0.74
	oxocol	0.022
	fine oxocol	0.034
	oleic acid	0.047
	oleyl alcohol	0.22
	C-20 guerbet alcohol	0.17

9. Less emulsible in aqueous phase
10. Ability to be sterilized or autoclaved and
11. High chemical stability

Of these criteria, the simultaneous achievement of biocompatibility and high distribution coefficient has been the focus of much attention. Kollerup and Daugulis (*14*) have generated a computer-based system that has screened 1362 solvents for their potential to combine biocompatibility and high distribution coefficient. They (*14*) chose oleyl alcohol as a good compromise between biocompatibility and efficiency. Roddy (*16*) has experimentally tested a variety of pure organic solvents for their potential use in ethanol-extraction processes (without regard to biocompatibility). Roddy (*16*) recommended tri-normal-butylphosphate (TBP) as the best all-around choice (not considering biocompatibility). Various solvents and their distribution coefficients are listed in Table 1. Although TBP ranks high on this list compared to other water-immiscible solvents, several groups (*11,12,18*) have reported it to be partially toxic for yeast.

If *in situ* solvent extraction of ethanol could be combined with cell immobilization, and if doing so relieved end-production inhibition, then a reactor with enhanced productivity could be developed. We have advocated the potential advantages of multimembrane reactors to do this (*19*). Sirkar's group (*20,21*) have also suggested an alternative formulation for a membrane-based reactor with solvent extraction.

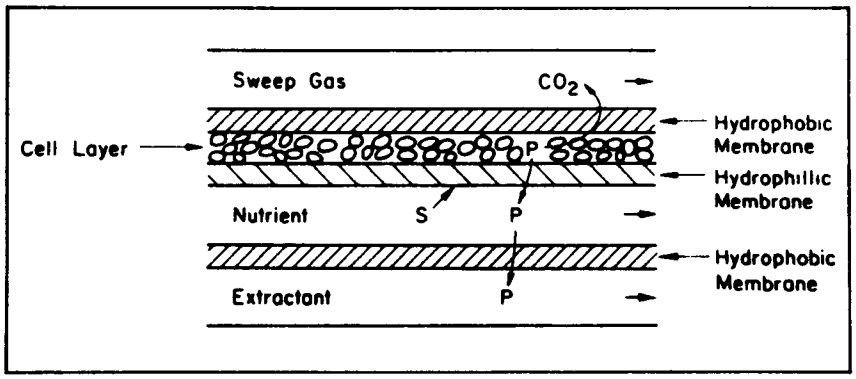

Fig. 1. A schematic diagram of the basic multimembrane reactor (from ref. *19*) is shown. In this case, S corresponds to glucose and P to ethanol. In more recent designs, the hydrophobic membrane between the gas and the cell layer has been removed and replaced with a liquid-level sensor. By cycling the gas-phase pressure, liquid can be pumped and in out of the cell-layer system. The high liquid-level sensor activates a valve to increase gas pressure, while the low level-sensor activates another valve switch, decreasing the gas pressure to less than the nutrient-level pressure. The hydrophobic membrane between the nutrient and extractant can be physically located in the same housing as the cell layer or in a housing separate from the cell layer with rapid recirculation of the nutrient stream between the two housings.

THE MULTIMEMBRANE-REACTOR CONCEPT

Figure 1 summarizes the original concept for a multimembrane reactor (*19*). A gas layer is included to promote the efficient removal of CO_2. Prior efforts on membrane reactors for ethanol production had encountered significant problems from gas pressure build-up resulting from CO_2 evolution (*1*). High gas pressures reduce nutrient flux into the cell chamber and can even cause the rupture of membranes or other matrices. The cell layer/nutrient membrane is critical to retention of a high cell mass. The nutrient/solvent membrane can play a critical role in preventing toxicity.

Cho and Shuler (*19*) demonstrated that TBP is not toxic to cells when present at saturating levels in fermentation media, but becomes toxic when cells are allowed to interact directly with emulsified droplets of solvent. Cho and Shuler (*19*) described this as "physical toxicity," which is now also called "phase toxicity." The MMR (multimembrane reactor) prevents phase toxicity by preventing direct contact of the solvent with the cells. If the pressure in the aqueous phase is greater than that in the solvent layer, and if a hydrophobic membrane is used, then solvent cannot enter the aqueous phase, and the aqueous phase will not enter the solvent layer if the pressure differential is less than the critical entry pressure into the hydrophobic pores of the membrane (usually 2–4 bars).

If the pressures are correctly controlled, TBP emulsification is prevented and toxicity is eliminated. Cho and Shuler (*19*) demonstrated that the use of a MMR allowed the complete conversion of a 200-g/L glucose-based medium at 30°C, whereas a similar system without *in situ* extraction could not. A batch reactor system with TBP, in which all phases were mixed, could not complete the fermentation because of TBP toxicity. Thus, the MMR system demonstrated protection against solvent toxicity.

However, the reaction rate was limited by the rate of diffusion of substrate into the cell layer and the rate of ethanol removal from the cell layer. Efthymiou and Shuler (*22*) introduced the concept of pressure-cycling to improve the productivity in a MMR. By cycling gas pressure so it is alternately greater than and lesser than the nutrient-side pressure, nutrient solution could effectively be "pumped" into and out of the cell layer. Such mixing greatly reduced or eliminated the differences in concentration between the cell layer and the nutrient layer, and supported a greater quantity of cells per unit of membrane area. One difficulty in operating this system for long periods was the occasional wetting of the gas/cell membrane with an ethanol–water mixture. The wet membrane would not allow gas passage.

This problem was solved by removing the gas/cell layer membrane and substituting a liquid-level control system in the flat-bed reactor. Steinmeyer and Shuler (*23*) have shown that such a reactor can be operated continuously for at least 3000 h with maintenance of a steady-state level of ethanol production. In the system with pressure cycling ethanol production exceeds the capacity for the solvent to remove it if the cell-retentive membrane and the extractive membrane are of the same size. A ratio of at least 3:1 for extractive to retentive membrane is required. These initial results were obtained with a glucose-based medium and yeast (*S. cerevisiae*).

Attempts at a molasses fermentation failed because of membrane fouling. However, the use of a corn starch hydrosylate gave satisfactory results. The use of *Zymomonas mobilis* proved unsatisfactory. The *Z. mobilis* cells formed filaments that retarded the removal of ethanol-rich liquid from the cell layer. The reduced effectiveness of the pressure cycle was more detrimental than any gain from the potential higher intrinsic fermentation rates for *Z. mobilis*.

A growth model for *S. cerevisiae* (*24*) has been constructed and applied to predicting MMR performance (*25*). Significant improvements in performance of pressure-cycled MMR are predicted when a hydrophilic retentive membrane with 0.45-μm pore size is used instead of a membrane with 0.22-μm pore size, but further increases in pore size do not give significant increases in performance. Additionally, significant improvements can be obtained if solvents with higher distribution coefficients can be found. Productivities range from about 1 to 6 g ethanol/h per 100 cm^2 of membrane area at 35°C. At this temperature the cells are particularly sensitive to ethanol inhibition.

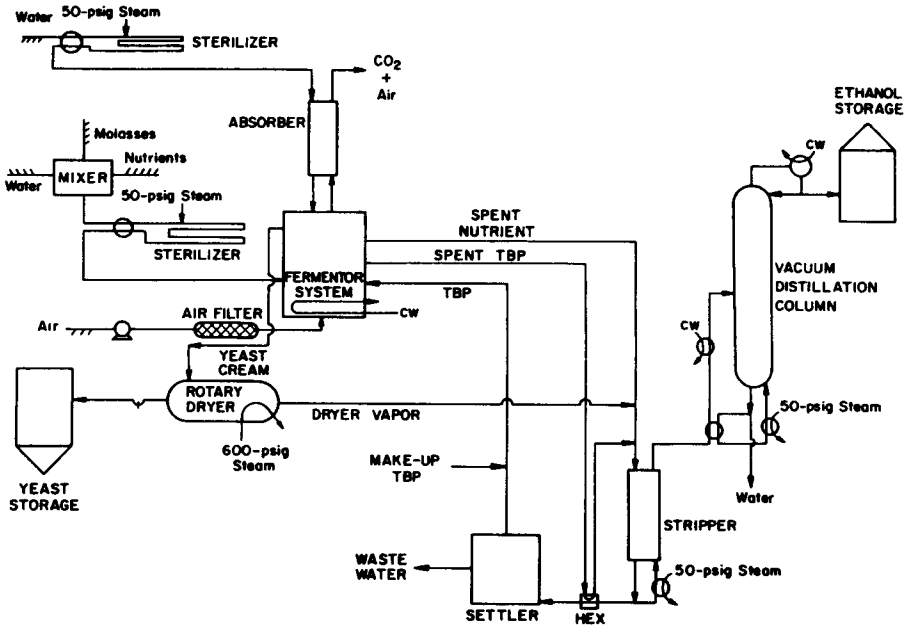

Fig. 2. Overall fermentation-ethanol plant-flow model for fermentation with selective ethanol removal using TBP.

However, the question of economic feasibility was not addressed in these earlier studies. The purpose of this paper is to suggest under what circumstances such a device might be economically attractive. The projected costs are given on a *relative* basis (compared to batch costs); the absolute values are not intended to be exact. This comparison of relative values leads to conclusions about the economic feasibility of the MMR system compared to the traditional batch-fermentation system.

ECONOMIC ANALYSIS

Maiorella et al. (*15*) have analyzed a wide variety of fermentation options for ethanol production. They have used a consistent basis to facilitate such comparisons. They found extractive fermentations to be the least expensive, but the analysis was based on a hypothetical extractant and did not specify or include the cost of the separator.

This discussion uses the same basis as Maiorella et al. (*15*), but substitutes our MMR system for their conventional batch reactors. Figs. 2 and 3 are the flow sheets that we propose for the MMR with two different solvents, TBP and Cyanex 923®. We have retained the same basic flow sheet that Maiorella et al. (*15*) used. Cyanex 923® (American Cyanamid Corporation, Wayne, NJ, USA) is a mixture of trialkyl phosphine oxides,

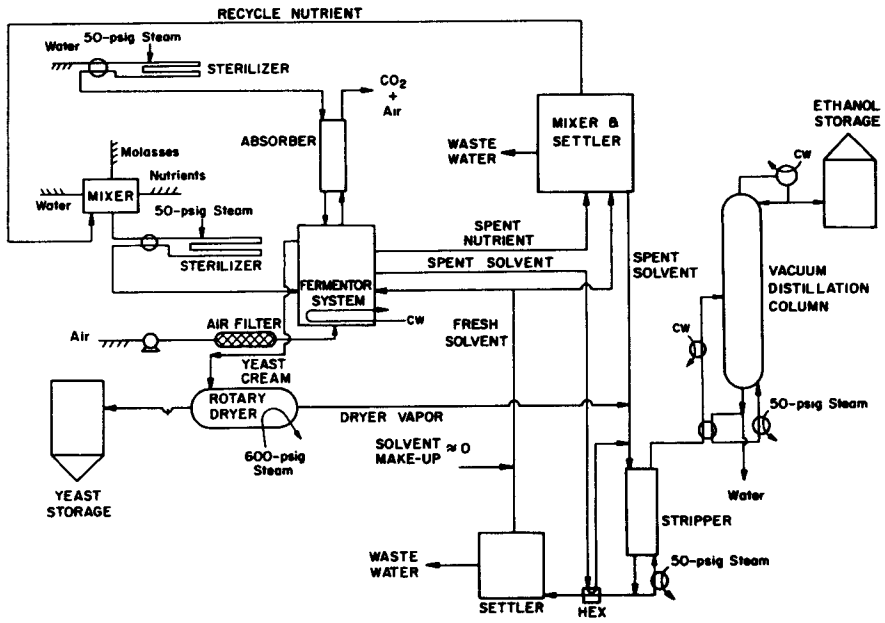

Fig. 3. Overall fermentation-ethanol plant-flow model for fermentation with selective ethanol removal using Cyanex 923®.

and the literature provided by the company suggests a distribution coefficient for ethanol of about 1.0 (*24*). Table 2 presents a summary of TBP and Cyanex 923® properties. Both flow sheets for a MMR show the elimination of the stillage-evaporation and the centrifuge steps, since yeast are retained in the reactor and the bottom stream from the stripper will contain little cell mass and, in some cases, no sugar.

A separator for the bottom stream to remove excess water is included. Because the recycled solvent must be cooled to fermentation temperatures and TBP to the stripper must be warmed, a heat exchanger with a 15°C approach is included.

In the Cyanex 923® case, the spent nutrient solution is not sent directly to the stripper, but is sent to a mixer-settler. The resulting aqueous phase is either recycled or sent to waste treatment. The ethanol-laden solvent is then sent to the stripper. The reason that the mixer-settler system is used with Cyanex 923®, and not with TBP, is the superior ability of Cyanex 923® to phase-separate.

Maiorella et al. (*15*) used 1×10^8 L/yr ethanol as the basis for production. Their analysis assumed a feed of molasses at 50% sugar. Since molasses cannot be used in the MMR, we have assumed a corn starch hydrolysate at 50% glucose. We have also used the same kinetic expressions used by Maiorella et al. (*15*), which apply at 25°C. Similarly, we have assumed 98.3% conversion of sugar and a yield of 0.434 g ethanol produced per 1.0 g of glucose consumed.

Table 2
Properties of TBP and Cyanex 923® Solvents

PHYSICAL AND CHEMICAL PROPERTIES OF TBP	
Structure: C_4H_9-O, O, P, C_4H_9-O, O-C_4H_9	
Molecular Weight:	267
Boiling Point:	289°C
Density:	0.97 g/mL
Solubility in Water	0.042 wt %
Saturation point of TBP in water:	0.39 g/L at 30°C
Distribution Coefficient:	0.54 at 25°C (in water)
	0.79 at 30°C (in medium)
Cost	$1.66/lb
PROPERTIES OF CYANEX 923® EXTRACTANT	
Average molecular weight	348
Trialkyl phosphine oxides	93%
Specific Gravity	0.88 (25 C)
Freezing Point	-5 to 2 C
Viscosity	0.04 Pa.s (25 C)
	0.014 Pa.s (50 C)
Boiling Point	310 C (6.66 kPA)
Solubility in water	< 10 mg/kg
Distribution Coefficients	1.0 (ethanol)
	5.2 (acetic acid)
	1034 (Phenol)
Miscible with common diluents.	
Cost	$6.50/lb

The TBP Option

TBP has been suggested as a good solvent for ethanol extraction (e.g., *16*). Its distribution coefficient appears to be greater in medium than in pure water. A distribution coefficient (K) of 0.79 in medium has been reported (*12*). In our experiments, we have observed values of 0.5–0.8. For this analysis we have used $K=0.79$.

For the TBP case, sufficient water is added to the carbon source to give 200 g/L glucose. The fermenter system contains two parts: In the first part, feed enters a reactor section without solvent extraction. The effluent for the first part is sent to a second section, where TBP is added. In the first part, the ethanol concentration is allowed to increase from 0 to 60 g/L. The system operates as a PFR (plug flow reactor), and the average degree

of inhibition of reaction is 15% (i.e., the average reaction rate is 85% of the maximum rate). In the second stage, *in situ* extraction is used to ensure that the ethanol concentration in the cell layer never exceeds 60 g/L.

The calculated membrane area for a 0.45-μm pore membrane was 11,000 m^2 in section 1 and 6,000 m^2 in section 2, assuming 0.04 g yeast/cm^2. Such cell density (0.04 g dry wt/cm^2) has been achieved in our experiments using a 0.22-μm-pore membrane (0.03–0.04 g/L is typical). With a pore size of 0.45 μm, the cell density may be even higher in consequence of a somewhat better nutrient supply. However, our experiments using a nutrient recycle system were restricted to pore size of 0.22 μm because of low-level leakage of yeast cells through the membrane. Such low-level leakage should not be a problem in a PFR. In our experiments, leakage was not detected until 20 h after the initiation of operation. A pore size of 0.45 μm is preferred because of more rapid nutrient exchange, which increases the reaction rate (*23*). The membrane area required to achieve a specified conversion is inversely proportional to cell mass. During continuous operation excess cell mass must be removed. A bleed from the cell layer can be driven by the gas pressure in the reactor. The bleed contains cells at a concentration equivalent to that of a yeast cream from a centrifuge (15% dry matter). The mass flow of yeast is about one-eighth of that in the batch process.

In the second reactor, 1.18 kg of water-saturated TBP/kg of nutrient solution is used. The exiting solvent stream is 91.1% TBP, 2.9% ethanol, and 6.0% H_2O. The mass-transfer coefficient across the hydrophobic nutrient/solvent membrane was estimated to be on the order of 1×10^{-4} cm/s in our bench-scale experiments. This is the mass-transfer coefficient in a flat-plate configuration with modest velocities; a well-designed module might increase the mass-transfer coefficient and decrease the required membrane area. With a mass-transfer coefficient of 1×10^{-4} cm/s, the required membrane area for solvent extraction would be 62,000 m^2.

The exit nutrient stream is 5.63% ethanol, 0.39% sugar, and 93.9% water, by weight. Both the exit nutrient and the solvent streams are sent to distillation. About a 20% reduction in water to the distillation column is achieved at the expense of increased volume to accommodate the TBP flow. Energy to the column is reduced as a result of less vaporization of water, but the added TBP flow adds a latent heat burden.

Tables 3 and 4 present the economic analysis for the TBP case. Although Maiorella et al. (*15*) state in the text of their article that the design is for 10^9 L of 95% ethanol/yr, the flow sheets and equipment sizes are based on 10^8 L of 95% ethanol/yr. Consequently, our system has also been designed for 10^8 L/yr. Maiorella et al. (*15*) used mid-1981 prices (Marshall Stevens Index=717) for equipment and raw materials; we have used the MSI to adjust our equipment prices to mid-1981 levels. Operation 24 h/d for 330 d/yr is assumed. Throughout the analysis we have used the same factors for estimating cost components as used by Maiorella et al. (*15*).

Table 3
Capital Cost Comparison – TBP Case

	BATCH	MMR-TBP at 25°C
Storage		
Sugar	$268,000	$268,000
Ethanol	$167,000	$167,000
Yeast	$247,000	$37,000
Conveyer Belt	$8,000	$2,000
Solvent	-	$57,000
	$690,000	$531,000
Fermentation		
Batch Fermenters & Agitators	$1,024,000	-
Fermenter Cooler	$28,900	$28,900
MMR (Housing)	-	$1,775,000
Seed Tanks & Agitators	$263,100	$32,900
Air Filter & Compressor	$47,000	$47,000
Feed Water Sterilizer	$86,100	$86,100
Feed Tank & Agitator	$33,300	$33,300
Centrifuge	$319,000	-
	$1,801,000	$2,003,000
Ethanol Recovery		
Absorber	$67,500	$67,500
Absorber-Water Sterilizer	$13,100	$13,100
Stillage Evaporator	$1,590,000	-
Rotary Dryer	$1,374,000	$254,300
Distillation	$341,000	$340,000
Bottoms Solvent/Water Separator	-	$57,000
Solvent Heat Exchanger	-	$168,000
	$3,386,000	$900,900
Total Purchase Equipment (PE)	$5,877,000	$3,434,000
Membrane Cartridges (MC)	-	$7,800,000
Fixed Capital Invest. (4.11 x PE + 1.2 MC)	$24,154,000	$19,025,000
Solvent Hold-Up Addition to Working Capital (SH)	-	$975,000
Total Capital Invest. (4.89 x PE + 1.43 (MC) + SH)	$28,739,000	$28,920,000

In Table 3, we have added to the capital cost of storage components the price of a 378,000-L carbon-steel tank. Although the make-up TBP stream is small (35 kg/h), a large tank is required because the solvent hold-up in the system is large and a large storage tank would be necessary during "down time."

In the fermentation section, the centrifuge is eliminated in the MMR system. The batch fermenters are replaced with the MMR, and only one of the eight seed-tank fermenters is retained. Estimating the cost of the MMR is difficult, since units of appropriate size are not now built. Based on conversations with a representative of Millipore Corporation (Bedford, MA), an industrial system for the 0.45-μm Durapore® membrane with pleated sheets (a variation of the flat-plate system) is available. The indus-

Table 4
Production Cost Summary – TBP Case

	BATCH c/L	MMR-TBP @ 25°C c/L
Raw Materials		
Nutrient Solution	1.110	1.110
Water	0.099	0.073
Carbon Source	34.700	34.700
Solvent Make-Up	-	0.491
Total Raw Materials	35.909	36.374
Utilities		
Power	0.592	0.132
Cooling Water	0.260	0.260
Steam (50 psig)	1.654	0.841
Steam (600 psig)	0.896	0.112
Total Utilities	3.402	1.344
Other Operating		
Operating Labor (OL)	1.348	0.513
Operating Supervision (15% OL) (OS)	0.202	0.077
Non-Membrane Maintenance (6% x 4.11 PE) (NMA)	1.460	0.847
Membrane Replacement (3 yr)	-	2.600
Non Membrane Operating Supplies (15% NMA)	0.220	0.127
Laboratory Charges (15% OL)	0.202	0.077
Total Other Operating	3.432	4.241
Direct Production Cost	42.743	41.959
Fixed Costs		
Depreciation (18 yr for 4.11 PE)	1.348	0.784
Property Taxes (3% FC)	0.730	0.704
Insurance (0.7% FC)	0.170	0.164
Total Fixed Costs	2.248	1.652
Plant Overhead (60% (OL + OS + NMA))	1.806	0.862
Manufacturing Cost	46.797	44.473
General Expenses		
Administrative (15% OL)	0.202	0.077
Dist. & Marketing (5% total production cost)	2.474	2.345
Total General Expenses	2.676	2.422
After-Tax Profit (15% ROI)	4.311	4.338
Income Tax	4.311	4.338
Yeast Credit	4.782(-)	0.598(-)
Steam Credit	0.268(-)	0.034(-)
	53.045	54.939
Waste Treatment	+0(?)	+(?)

rial unit can accommodate up to eighteen 30-in. (76.2 cm) cartridges. Each cartridge contains 21 ft^2 of membrane (1.95 m^2). The housing costs about $7295 and 18 cartridges cost $5770. To give 17,250 m^2, about 492 such units would be required. The cost of the membrane housing was extrapolated from this situation by assuming that the cost of the housing would scale to an exponent of 0.6 and that 20 units would be satisfactory.

The cost of membrane cartridges was assumed to be scale-independent. Thus, the housing cost for the system was estimated to be $(492/20)^{0.6}$ $\$7,295 \times 20 = \$997,000$, which was converted to 1981 costs as follows: $\$997,000 \times (717/903) = \$790,000$. The cost of the membrane cartridges was $2,840,000. Since membrane costs have fallen rapidly since 1981, current prices were used without adjustment.

In addition to the retentive membrane, extractive membrane is required. Membrane and housing prices were discussed with technical representatives from Hoechst-Celanese Corporation (Charlotte, NC) and from Niro-Atomizer Food & Dairy Corporation (Hudson, WI) concerning hollow-fiber and spiral-wound molecules. Although in the reactive portion of the system a "thick" cell layer (ca. 0.5 cm) is required, membrane spacing can be much closer in the extractive part of the process. Currently these membrane units are sold in basic modules with 3–28 m^2 of surface area. Apparently consideration is being given to larger systems in which cost/unit membrane might well decrease. Based on current technology, costs are about $\$100/m^2$, with a little more than 80% for membrane cartridges or elements and a little less than 20% for the housing. For 62,000 m^2, a membrane-cartridge cost of $4,960,000 is estimated. The housing cost is $1,240,000, which converts to a 1981 cost of $985,000. The total membrane-housing cost for both types of membrane unit is then $1,775,000. The cost of the total permanent equipment in the fermenter section increases slightly (by 11.2%).

The membrane-cartridge cost is treated separately, since the factor of 4.11 to convert purchased equipment cost into fixed costs would not be applicable to the membrane cartridges. A 20% installation charge is applied (10–20% is standard), and the membrane-cartridge cost is then included in the fixed-cost estimate. It should be noted that the membrane cost *per se* is $< 20\%$ of the cost of the membrane cartridges. A system specifically designed for ethanol production might show a further reduction in cost.

The above analysis is based on commercially available membrane cartridges. It involves a sequence of reactive units followed by a sequence of reactive units coupled to extractive units, in which the coupling is similar to our recent bench-scale experiments (23). Small-scale multimembrane units have been manufactured, and the design of locally integrated membrane units directly suitable to a MMR concept is feasible, if the demand for such a system would warrant its construction.

In the recovery section, the stillage evaporator is totally removed, and the rotary dryer is down-sized to one-eighth of original capacity and cost is reduced by $(1/8)^{0.6}$. The distillation system has increased liquid downflow with decreased vapor up-flow because of a reduced quantity of water in the system. An extra heat exchanger and bottom solvent/water separator is added. Capital costs in the recovery section are reduced very substantially ($\$3.39 \times 10^6$ to $\$0.9 \times 10^6$).

The fixed capital is calculated as 4.11 times the cost of the permanent equipment plus 1.2 times the membrane-cartridge cost. This method treats membrane-cartridge cost in a manner analogous to that by which catalyst costs are often calculated. To convert to total capital cost, fixed costs are multiplied by 4.89/4.11 plus the solvent hold-up costs. Solvent hold-up cost is a working-capital item; since we are comparing to the traditional process in which no solvent is used, we decided it would be fairer to include this as an addition to the normal estimate of total capital cost.

In Table 4 we have adopted the conventions suggested by Maiorella et al. (*15*). We have used the labor input they suggested for extractive fermentation processes (6.15 workers/shift vs 16.15 workers/shift). We have assumed a 3-yr life for membrane units, which is at the upper end of what might be reasonably expected. In our experience with 3000 h of continuous operation, membrane integrity was maintained with no significant loss of effectiveness. For 10^8 L/yr, the MMR with TBP is slightly more expensive than the traditional process ($54.9 vs $53/L), largely because of the high cost of membranes. Also, the cost for waste treatment is not included. Maiorella et al. (*15*) believe that waste-treatment costs in their design would be negligible as a result of recycling nutrient and stillage streams, with all waste solids going to animal feed. In the MMR case, waste streams totaling 96,700 kg water/h, 400 kg glucose/h, and 35 kg TBP/h would need to be treated. The presence of solvent, particularly TBP, may raise regulatory issues not considered here.

The Cyanex 923® Option

This design is more speculative, since we have not had the resources to operate a MMR with Cyanex 923®. Simple shake-flask studies have shown Cyanex 923® to be nontoxic (considering both phase and molecular toxicity) for yeast. Our attempts to estimate the distribution coefficient have been somewhat inconsistent; most values have been between 0.4 and 0.7, although one value was at 1.4. A value of 1.0 was estimated from the literature available to us (*26*) and was used in the design. Phase separation was apparent within 10–15 min after removing the shake flasks from the shaker, which was much more rapid than that observed in shake flasks with TBP.

The design was much like that for the TBP option, and costs are summarized in Tables 5 and 6. Because of its apparent biocompatibility, the separate extractive-membrane unit used in the TBP case was removed, and direct injection of the solvent into the nutrient stream was envisioned. A 250 g/L feed was used instead of 200 g/L because of the reduced sensitivity of the system to extractive-membrane cost. The slightly more concentrated feed results in somewhat greater inhibition of the reaction, leading to a slightly larger retentive-membrane area than in the TBP case (17,960 m^2 instead of 17,250 m^2). This would require 511 current units. If

Table 5
Capital Cost Comparison – Cyanex Case

	BATCH	MMR-Cyanex at 25°C
Storage		
Sugar	$268,000	$268,000
Ethanol	$167,000	$167,000
Yeast	$247,000	$37,000
Conveyer Belt	$8,000	$2,000
Solvent	-	$27,000
	$690,000	$501,000
Fermentation		
Batch Fermenters & Agitators	$1,024,000	-
Fermenter Cooler	$28,900	$28,900
MMR (Housing)	-	$810,000
Seed Tanks & Agitators	$263,100	$32,900
Air Filter & Compressor	$47,000	$47,000
Feed Water Sterilizer	$86,100	$86,100
Feed Tank & Agitator	$33,300	$33,300
Centrifuge	$319,000	-
	$1,801,000	$1,038,000
Ethanol Recovery		
Absorber	$67,500	$67,500
Absorber-Water Sterilizer	$13,100	$13,100
Stillage Evaporator	$1,590,000	-
Rotary Dryer	$1,374,000	$254,300
Distillation	$341,000	$141,000
Mixer/Settler	-	$105,000
Bottom Solvent/Water Separation	-	$22,000
Solvent Heat Exchanger	-	$225,000
	$3,386,000	$828,000
Total Purchase Equipment (PE)	$5,877,000	$2,367,000
Membrane Cartridges (MC)	-	$2,954,000
Fixed Capital Invest. [(4.11 x PE) + 1.2 MC]	$24,154,000	$13,273,000
Solvent Hold-Up Addition to Working Capital (SH)	-	$3,906,000
Total Capital Invest. [(4.89 x PE) + 1.43 MC + SH]	$28,739,000	$18,773,000

we still specified 20 units and the costs scale similarly, we would have a housing cost of $810,000. The membrane cost is $2,954,000.

In the recovery section a mixer-settler is added. A mixer-settler was not used in the TBP case because of the difficulty in gravity separation of TBP and fermentation broth. Four equilibrium stages result in a residual ethanol level of about 0.3% (by weight) in the aqueous stream. The feed to the distillation column contains 264,800 kg/h solvent, 15,800 kg/h water, 9,860 kg/h ethanol, and the vapor stream from the dryer, which is 1,340 kg/h H_2O and 140 kg/h ethanol. The bottom solvent/water separator has a 12-min residence time compared to the 2-h time used for the TBP case. Because the solubility of Cyanex 923® in water is so low, the make-up stream is nearly zero (0.25 kg/h). In developing the costs of the mixer-

Table 6
Production Cost Summary – Cyanex Case

	BATCH c/L	MMR-Cyanex @ 25°C c/L
Raw Materials		
Nutrient Solution	1.110	0.350
Water	0.099	0.004
Carbon Source	34.700	34.700
Solvent Make-Up	-	0.010
Total Raw Materials	35.909	35.064
Utilities		
Power	0.592	0.132
Cooling Water	0.260	0.260
Steam (50 psig)	1.654	0.420
Steam (600 psig)	0.896	0.112
Total Utilities	3.402	0.924
Other Operating		
Operating Labor (OL)	1.348	0.513
Operating Supervision (15% OL) (OS)	0.202	0.077
Non-Membrane		
Maintenance (6% x 4.11 PE) (NMA)	1.460	0.796
Membrane Replacement (3 yr)	-	0.985
Non Membrane		
Operating Supplies (15% NMA)	0.220	0.119
Laboratory Charges (15% OL)	0.202	0.077
Total Other Operating	3.432	2.567
Direct Production Cost	42.743	38.555
Fixed Costs		
Depreciation (18 yr for 4.11 PE)	1.348	0.737
Property Taxes (3% FC)	0.730	0.398
Insurance (0.7% FC)	0.170	0.093
Total Fixed Costs	2.248	1.228
Plant Overhead (60% (OL + OS + NMA))	1.806	0.832
Manufacturing Cost	46.797	40.615
General Expenses		
Administrative (15% OL)	0.202	0.077
Dist. & Marketing (5% total production cost)	2.474	2.170
Total General Expenses	2.676	2.247
	BATCH c/L	MMR-TBP @ 25°C c/L
After-Tax Profit (15% ROI)	4.311	2.956
Income Tax	4.311	2.956
Yeast Credit	4.782(-)	0.598(-)
Steam Credit	0.268(-)	0.034(-)
	53.045	49.929
Waste Treatment	+0(?)	+(?)

settler component, a carbon-steel unit was chosen; the system would cost approximately twice as much if stainless steel were required. Capital costs and energy costs are much reduced in the recovery section.

The overall capital investment is calculated using the same reasoning as used in the TBP case. The cost of Cyanex 923® is four times the cost of TBP, which increases solvent hold-up costs significantly.

Table 7
Comparison of Final Product Cost
For Several Process Options For Ethanol Production (mid-1981 Basis)

Process	Final Product Cost ¢/L	Fraction of Batch Process
Batch+	53.05	1.00
CSTR+	51.29	0.97
Recycle CSTR+	49.06	0.92
Plug Flow+	49.11	0.93
Perforated Plate Column+	52.34	0.99
APV Tower+	48.71	0.92
Selective Membrane+	47.26	0.89
Flash+*	44.46	0.84*
Extractive+*	43.94	0.93*
TBP	54.94	1.04
Cyanex 923	49.93	0.94

+From reference 15

*These costs do not include in the costs associated with the separator

The operating costs follow the same pattern as for the TBP case. With Cyanex 923®, we project a reduction in cost with respect to the traditional case (49.9 vs 53 ¢/L) and the TBP case (54.9 ¢/L).

Because of internal recycle and more concentrated reactor feed, the waste-treatment costs in this option may be less than in the TBP case. We project a composite waste stream with 26,000 kg/h water, 30 kg/h ethanol, 80 kg/h sugar, and 0.25 kg/h Cyanex 923®.

DISCUSSION

The costs of the TBP and Cyanex 923® are compared in Table 7 with the costs projected by Maiorella et al. (*15*) for several other process options. These costs projected here are higher than their estimates for selective membrane, flash, or extractive fermentations. However, they explicitly excluded in those estimates the costs associated with the separator. Also, they assumed in the extraction case a value of 6 for the ratio of ethanol concentration in the separator-concentrated product stream to its concentration in the dilute product stream. This ratio is not achieved in the TBP case, although in the Cyanex case, if we consider only the ethanol-to-water-content ratio, a factor of approximately 6 is achievable, although it is less if solvent is considered.

The designs reported here were not optimized; rather, they are representative estimates that are intended to be neither too conservative nor too optimistic. The primary reason that the MMR option is not more at-

tractive is the relatively high cost of membranes. However, the costs of membrane units have decreased dramatically in the last 15 yr (from about \$100/ft^2 (\$1000/m^2) to \$10/ft^2 (\$100/m^2)). Companies are planning membrane units that will be larger and should drive costs down even further. Thus, a MMR may be an economically attractive proposition in another decade or so.

Also, the energy consumption required in the MMR cases represent a significant reduction of indirect energy expenditures. With TBP a 60% reduction—and with Cyanex a 73% reduction—was achieved compared to Maiorella et al.'s (*15*) batch-reactor case with yeast recovery. Fermentation ethanol becomes particularly important in the event of an overall energy crisis, in which case these energy savings would be magnified in importance.

It is also interesting to consider what effect scale would have on the economic comparison of the TBP and batch systems. Most equipment costs scale roughly to a power of 0.6, but membranes and solvent costs scale to an exponent of 1.0. If we take the analyses in Tables 3 and 4 and scale to 10^7 L/yr ethanol (95% by weight) using a factor of $(0.1)^{0.6} = 0.2512$ to multiply permanent equipment costs and a factor of 3.3 for labor costs per liter of product, we find that the cost per liter of product are 80.68 ¢/L for the batch case and 69.65 ¢/L for the TBP case. At about 7×10^7 L/yr the costs of the TBP and batch cases would be equal. Thus, alcohol production at a small scale would favor the MMR and TBP system, which could be important for cases in which a cheap raw material is available in moderate quantities, but collection costs prohibit collection of large quantities at a competitive cost.

Another limitation of the MMR system is that *Zymonomas mobilis* may not be used effectively (*23*), although traditional reactor systems can use *Z. mobilis*. Thus, the economic comparison of the MMR system with yeast to other systems with *Z. mobilis* may be less favorable to the MMR system than comparisons to traditional units with yeast.

CONCLUSIONS

1. The MMR concept allows the use of solvents for *in situ* extraction when the solvent shows "phase toxicity" but not "molecular toxicity."
2. A MMR can be operated for extended periods with performance sustained at acceptable levels.
3. The MMR with TBP for ethanol production is not economically attractive at levels of 10^8 L/yr or larger. However, if membrane costs were reduced severalfold, the process would become attractive.
4. Cyanex 923® is a potentially interesting solvent for ethanol extraction; a process based on this solvent could be attractive.

However, very little experience with this solvent has been reported and operational problems associated with its use cannot now be predicted.

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