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Biocatalysis Research Activity Potential Membrane Applications to Biocatalyzed Processes Assessment of Concentration Polarization and Membrane Fouling

By
J D. Ingham

February 1983

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California Institute of Technology
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Potential Membrane Applications to Biocatalyzed Processes: Assessment of Concentration Polarization and Membrane Fouling

J.D. Ingham

February 1983

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Abstract

Separation and purification of the products of biocatalyzed fermentation processes, such as ethanol or butanol, consumes most of the process energy required. Since membrane systems require substantially less energy for separation than most alternatives (e.g., distillation) they have been suggested for separation or concentration of fermentation products. This report is a review of the effects of concentration polarization and membrane fouling for the principal membrane processes: microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and electrodialysis (ED) including a discussion of potential problems relevant to separation of fermentation products.

It was concluded that advanced membrane systems may result in significantly decreased energy consumption. However, because of the need to separate large amounts of water from much smaller amounts of product that may be more volatile than water, it is not clear that membrane separations will necessarily be more efficient than alternative processes. To establish the most energy-efficient, economically effective separation technology for any specific fermentation process, it will be necessary to make detailed energy-economic assessments of alternatives, followed by experimental validation and engineering development.

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Introduction

Separation and purification of the products of biocatalyzed fermentation processes consumes most of the process energy required. (For example, Cf. Ref 1). Advances in genetic engineering should yield increased energy efficiency through higher tolerance to products and organic solvents in fermentation reactors; however, supportive advances in separation technology will still be very important in the minimization of total energy consumption. Since membrane systems require substantially less energy than most alternative processes, they have been suggested for separation or concentration of primary fermentation products and may also be applicable to separation and recovery of relatively high-cost byproducts or catalysts (e.g., riboflavin, enzymes or cofactors). Therefore, this report was prepared to aid in the future development of energy-efficient biocatalytic processes for production of industrial specialty or commodity chemicals, as part of the Energy Conversion and Utilization Technologies (ECUT) Biocatalysis Research Activity at JPL.

Most types of membrane separation processes have been described in previous review papers by Strathmann (2), Lonsdale (3, 4) and others. These include microfiltration (MF) ultrafiltration (UF), reverse osmosis (RO), dialysis, electrodialysis (ED), and gas separation.

MF, UF, RO, and gas separation are driven by pressure differences applied across the membrane. MF membranes are symetrical with 0.1 to 10 μm pores, and operate by a sieving mechanism at pressure gradients of 0.1 to 2 bars. The main application is to produce sterile, particle-free water. UF is similar, but asymmetric membranes with smaller pores (< 0.3 μm) and pressure gradients of 0.5 to 5 bar are normally used to retain various colloids and macromolecules. An asymmetric membrane is one in which separation is controlled at the feed side of surface of the membrane because the pore diameters (or effective pore sizes for solution-diffusion membranes) at that surface are smaller than the downstream pore diameters. RO membranes are generally asymmetric "skin type" membranes in which the mechanism is via solution diffusion in the feed-side skin or surface, driven by a higher pressure gradient (20 to 100 bar). The main application is desalination and separation of other specific solutes. Dialysis is driven by a concentration gradient and the main application is in blood purification for the treatment of uremia. Cation and anion exchange membranes are used in ED, where separations are driven by an electrical potential gradient to remove ions from aqueous solutions. Gas separations are driven by hydrostatic pressure gradients via a solution-diffusion mechanism to separate and concentrate components of gas mixtures.

Concentration Polarization

Concentration polarization, defined as an increase in concentration of the retained components near the membrane surface as permeation proceeds, can result in a decrease in permeation rate in many membrane processes. In MF, concentration polarization is normally accepted because the permeation rate is relatively high at low pressure gradients, although cross flow, back washing or other cleaning methods may be employed to minimize or remove retained particles. In dialysis, concentration polarization is normally not a problem because diffusion in the relatively thick membrane is slow compared to flow processes at the membrane surface. Similarly, in gas separations, diffusion is orders of magnitude lower in the membrane than in the gas phase, so the effects of any concentration polarization are negligible.

However, concentration polarization and consequent membrane fouling may cause serious problems in ultrafiltration, reverse osmosis and electrodialysis. For example, it has been calculated that feed containing only 100 ppm of calcium carbonate could deposit 300 g of precipitated carbonate in an 8" diameter RO hollow fiber module within one hour (5).

Membrane Fouling in Reverse Osmosis

Following major advances in membrane system development, such as development of cellulose acetate hollow fibers by Mahon, et al (6, 7, 8) and high-flux "skinned" asymmetric membranes by Loeb and Sourirajan (9), it was believed that membranes would be used in preference to many alternative, established separation methods (e.g., distillation, freeze concentration, extraction). However, experiments on various industrial waste streams, salt solutions, fermenter supernatant, food products and sludge water (10) showed that two problems seriously affect the general applicability of membrane systems: concentration polarization and membrane fouling. Because of the importance of these effects they have been investigated in considerable theoretical and empirical detail, and fouling of RO membranes has been extensively reviewed by Potts, Ahlert and Wang (11).

Concentration polarization is the presence of a higher concentration of rejected species at the membrane surface than in the initial feed or bulk solution, and the concentration polarization modulus, C_p is equal to C_s/C_b, where C_s is the surface concentration and C_b is the bulk concentration as indicated in Figure 1. In agreement with the usual solution-diffusion models for RO transmembrane flux, C_p is proportional to the net pressure across the membrane. Since osmotic pressure is increased at higher C_p (and opposes the

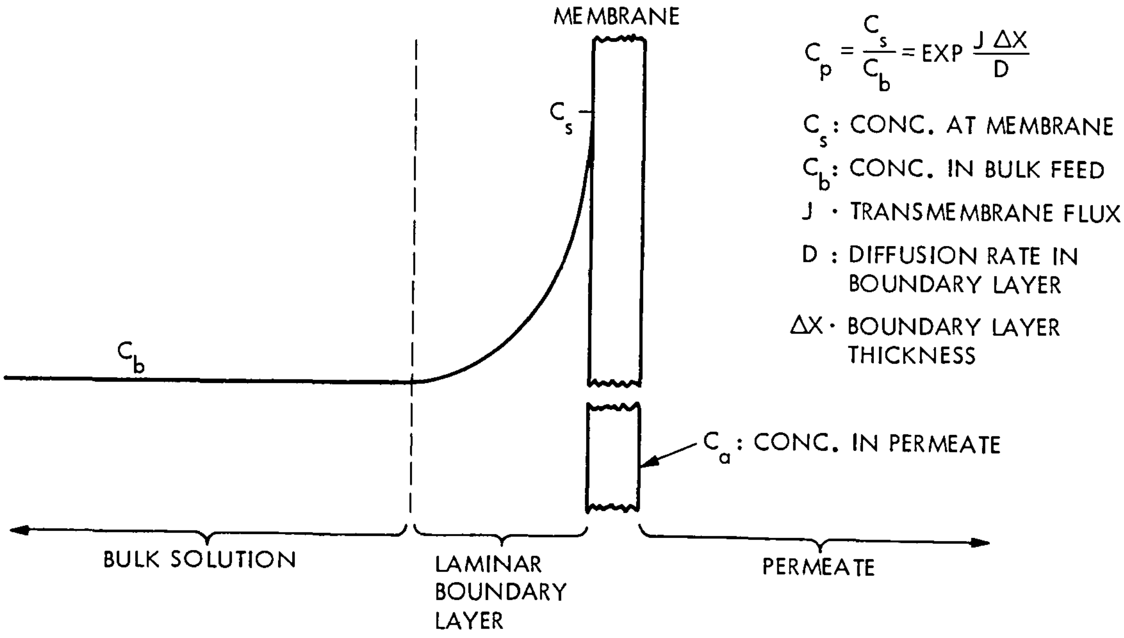

Figure 1. Concentration Profile in Membrane Processes

direction of flow) transmembrane flux is correspondingly decreased. Furthermore, solute flux increases because it is directly proportional to the change in solute concentration across the membrane (C_s-C_a, where C_a is the solute concentration in the permeate). Concentration polarization increases fouling because the concentrations of substances that result in fouling are higher at the surface and their upper solubility limits may be exceeded, causing them to precipitate.

Equations have been developed that show that high-flux and low-feed velocity increase concentration polarization, for example (12):

$$C_p = \exp \frac{2V \, (\upsilon/D)^{2/3}}{f \, U_b} \qquad (1)$$

Eq. (1) applies to turbulent flow in round tubes, where V is the volumetric flux of solvent through the membrane, $(cm^3/cm^2)/s$; υ is kinematic viscosity, cm^2/s; D is the diffusion coefficient of solute in solvent, cm^2/s; f is the Fanning friction factor and U_b is the bulk velocity, cm/s. The friction factor can be increased by increasing turbulence to decrease C_p. High molecular weight solutes increase C_p because they have low diffusion rates, high solution viscosities and lower bulk velocities. But higher molecular weight is advantageous in UF, dialysis and RO because the rejection or maximum limit of concentration is higher for higher molecular weights. For example, the upper limit for concentration of dextrose by RO is about 22 wt %, but for soluble coffee (with components of higher molecular weight) the limit is about 34 wt % (13). Equations have also been developed for laminar flow to predict solute buildup with tube length and with tube diameter for single and multiple-stage operation for design calculations (14).

Membrane fouling is essentially coating or plugging of the membrane by components in the feed. Although the normal consequence of fouling is a decrease in flux, there may also be a decrease in component rejection, with or without a flux decrease (15). Foulants include inorganics, particulates, dissolved organics and biological reactants.

Dissolved inorganics can easily form scale if their solubility limit is exceeded at the membrane surface. Therefore, acid or chelating agents are commonly used to avoid scaling from calcium salts in RO waste water treatment. However, if the rejected species is the product to be recovered, it may not always be practical to utilize conventional additive pretreatment methods.

Among particulates, it has been found that those >5 μm, which include settleable solids, do not significantly contribute to fouling of RO membranes (16) and Sugahara, et al, have concluded that particles smaller than 0.45 μm (and dissolved solids) are the most serious foulants (10). In some cases, humic acids and organic colloids are more likely foulants at lower feed pH (17). Biological products: carbohydrates, proteins, cells, cell debris, humic acid and tannins, whether present as colloids or dissolved, tend to cause severe fouling. Biological reactants can degrade membrane performance either by fouling or by biocatalytic attack on the membrane. The latter can be particularly serious for cellulose acetate membranes.

Although there has been a considerable effort devoted to studies of theoretical mechanisms of fouling by dissolved and colloidal organics, there is currently no coherent theory available. Some observations that can be used to judge the extent of fouling expected are as follows:

1. High rejection membranes do not foul us easily as "loose" membranes.
2. In some cases, asymmetric membranes can be reversibly cleared of fouling by mechanical surface scrubbing.

3. Colloidal particles may deposit on membranes to provide sites for adsorption and dissolution of organic solutes, to decrease flux (16).
4. Reversible or irreversible fouling may occur on the membrane surface or within the membrane.
5. As salt content increases, colloidal stability may decrease leading to coagulation and fouling (18).

For ultrafiltration, a model has been developed that shows that fouling occurs when membrane permeation velocity is greater than radially directed particle lift velocity (19). RO flux decline has been found to correspond to an empirical expression:

$$m = \log (F_t/F_0)/\log (t/t_0)$$

where m is the flux decline index and F_t and F_0 are the flux at time t and the initial flux at time t_0, respectively (20).

Concentration Polarization in Ultrafiltration

Fluxes are normally very high for ultrafiltration relative to reverse osmosis (~ 100 vs. 15 to 30 gal/ft^2/day for RO). The components that are separated are particles or macromolecules (molecular weight > 20,000) with low diffusivities. As the hydrostatic pressure and flux is increased, gel or a filter cake forms on the membrane surface as a result of concentration polarization. As soon as the gel layer is formed the concentration gradient between the membrane surface and feed solution reaches a maximum value and an equilibrium is established with back diffusion and solute movement toward the membrane becoming equalized. If the pressure is then increased, more solute will be transported to the membrane surface than will diffuse back to the bulk solution. Since the pressure required for a given flux depends on the gel layer thickness, the rate of filtration becomes independent of the hydrostatic pressure, i.e., an increase in pressure causes only an increase in gel thickness (21, 22, 23). Therefore, the optimum pressure is the pressure where flux becomes independent of pressure and a gel layer just begins to form. In this case there is normally no contaminant membrane fouling.

Concentration Polarization in Electrodialysis

Electrodialysis is a relatively specialized membrane process for removing ions from one series of compartments and concentrating them in a second series of compartments (Figure 2). For example, the first compartment can be the anode compartment enclosed by a cation-selective membrane. When current is applied the cations will be repelled by the anode and pass through the membrane to an ion-concentrating cell. The opposite side of the concentrating cell is an anion-selective membrane through which anions pass from the central ion-depleting cell because of the higher concentration of cations in the ion-concentrating cell. The cathode-side of the cell is similar, except that the charges are reversed. Electrodialysis is widely used for desalination, although installed plant capacity is much higher for RO systems (24). The operational effects of concentration polarization on defined feeds have been clearly established (2) and can be accommodated by appropriate system design. There have been problems with fouling, particularly at the anion-exchange membrane, apparently caused by the change in pH that occurs on the brine side of the membrane to cause increased resistance across the stacks. However, the effects of fouling can be nearly eliminated by reversing roles of the the concentrating and diluting compartments with simultaneous polarity reversal every 15 to 30 minutes (25). This process is known as electrodialysis reversal (EDR) and minimizes fouling to the extent that the only feed pretreatment normally required for high salinity water is cartridge filtration. The electrodes and membranes are also cleaned in place periodically with dilute acid. Since the membranes are expected to last of the order of seven years, system disassembly and overall maintenance costs may

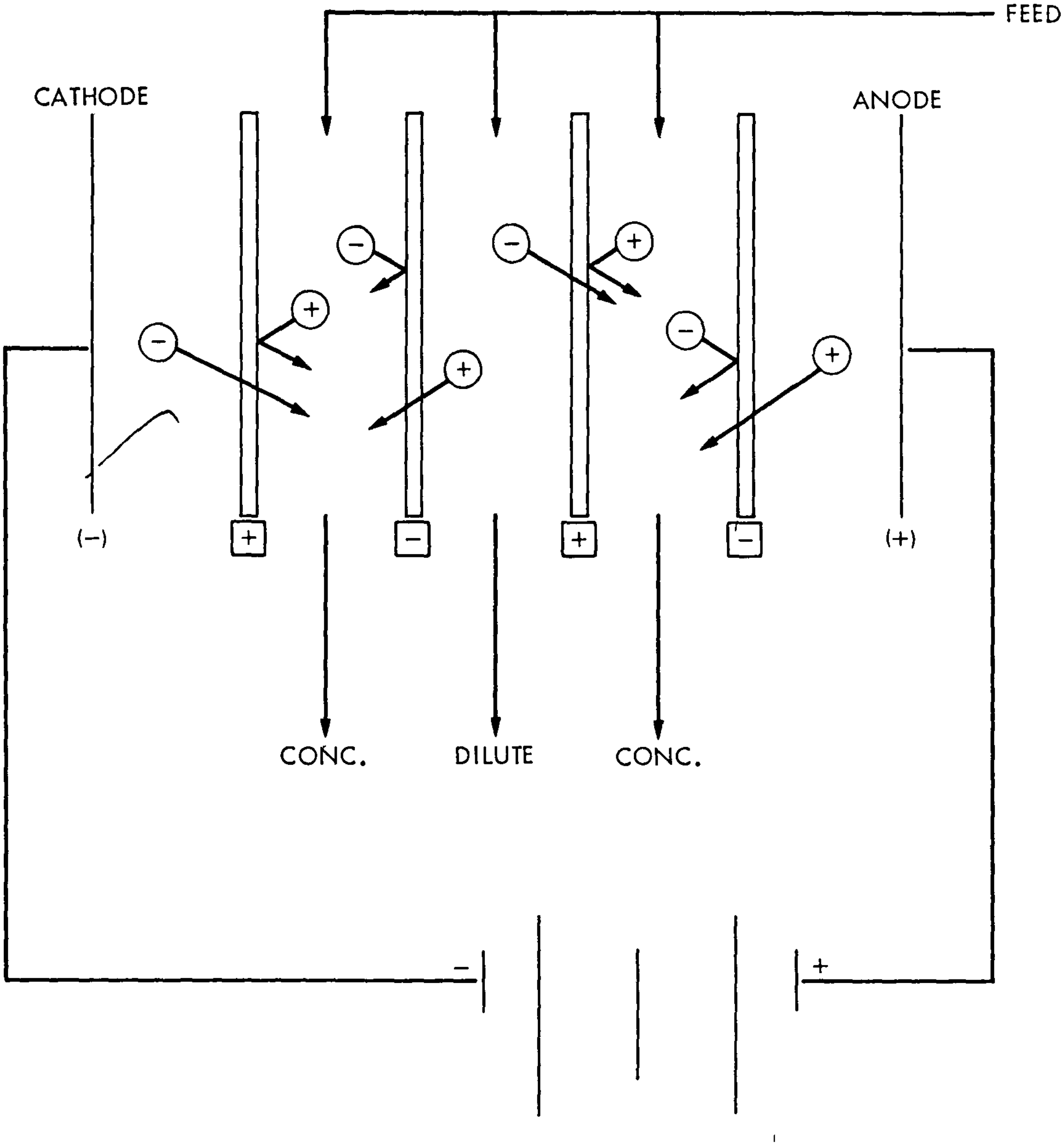

Figure 2. Schematic of Electrodialysis (ED) Membrane System (Alternating Anion-exchange |+| and Cation-exchange |−| Membranes).

be less than for RO (26). Energy consumption for desalination by RO or EDR is comparable, although EDR consumption is more sensitive to feed concentration (27).

Prediction of Fouling in Membrane Systems

Prediction of membrane fouling on a theoretical basis has not reached an advanced stage, partly because of the large number of feed, membrane and operational parameters and complex interactions that influence the extent of concentration polarization and fouling. Considering the range of applications and characteristics of various membrane processes, the most severe problems are encountered in RO, and the minimization and avoidance of fouling may account for up to 30% of RO processing costs.

Many empirical feed parameters such as mineral analysis, COD, UV absorbance at 275 nm, turbidity, electrophoretic mobility (zeta potential), concentration of hydroxylated aromatics or humic acids and silt density index (SDI) have been examined as a means of predicting fouling for the design of RO facilities (28). Of these, only SDI has been found to be somewhat acceptable.

The SDI test was originated by DuPont and utilizes a 0.45 μm Millipore filter, which is actually an ultrafiltration membrane. The test does not simulate RO conditions. The RO feed is passed through the filter at 30 psi (207 KP_a). The time required to collect the first 500 ml of filtrate is t_i. Fifteen minutes after the start of the test another 500 ml of filtrate is collected and the time required is t_f. The plugging factor ($\% P_{30}$) is calculated from:

$$\% P_{30} = 100\ (1-t_i/t_f)$$

$$\text{and SDI} = \frac{\% P_{30}}{15 \text{ min}}$$

The range of SDI values is 0 to 6.67, and the value is a sensitive measure of colloidal product concentration. There are some variations of this test, e.g. decreasing the time period from 15 to 5 minutes, but then the measurement results are not comparable. DuPont and other membrane manufacturers often set maximum allowable SDI values for their membrane systems. For DuPont hollow fiber permeators the maximum is 3.0 (29). As a consequence the degree of pretreatment of feed required may be appreciable. For example, tap water may have an SDI so high that it cannot be measured, and even deionized water may have an SDI > 4.5. Fortunately, some RO systems can be operated effectively at SDI's >5.0, but pretreatment and frequent cleaning are almost always required. It appears that the relative success of the SDI test as a means of "predicting" RO operational fouling characteristics may be largely a result of the low maximum allowable SDI values prescribed by membrane system manufacturers. In actual practice, the effects of feed on membrane operational characteristics are normally determined by laboratory, pilot-plant and full-scale tests and operations. However, there has been some recent progress on validation of a model based on the Modified Fouling Index (MFI) which is directly proportional to the fouling potential of the water (30).

Feed Pretreatment and Membrane Module Cleaning

Maximum feed pretreatment to minimize fouling is required for RO in comparison with other membrane processes, particularly if spiral wound or hollow fiber configurations are used. These low-cost, high-area-density systems cannot normally be disassembled for cleaning or fouled membrane replacement. The other two higher-cost, lower-area-density configurations are tubular or plate-and-frame. In fact, spiral wound or hollow fiber systems are used mainly for desalination, and tubular or plate-and-frame systems for most applications where the feed is likely to cause extreme fouling, and may not always be susceptible to pretreatment. RO has been used for treatment of sewage effluent (30, 31, 32), pulp and paper effluents (33, 34), milk (35, 36, 37), fermentation broth (37), and plating solutions (38, 39).

Pretreatment is most necessary for hollow fiber systems, and can account for as much as 50% of the total process costs (40) although costs are normally less than this. A typical pretreatment system may include chemical clarification with lime, alum or ferric chloride, media (e.g. sand) filtration, cartridge filtration, treatment with activated carbon, chlorination, dechlorination, acidification, and chemical treatment to minimize scaling. Ultrafiltration may also be used (41). However the cost is relatively high, and where dissolved organics or microcolloids are the principal foulants, it may be ineffective. An iodine shock treatment for 30 minutes per day to eliminate biological fouling has allowed continuous operation of a hollow fiber RO plant for more than eight months (42). Some current hollow fiber modules utilize an aromatic polyamide membrane, which is degraded by chlorine, but can withstand iodine shock treatment.

As indicated previously, EDR requires substantially less pretreatment of feed than RO and may be preferred for desalination if chemical costs are high, as in Bahrain, where chemical costs are ten times as much as in the United States (26).

Physical or chemical cleaning of RO modules is a normal operation in most plants. Physical methods can include backwashing, depressurization followed by flushing with water at high velocity, and sponge-ball cleaning. Backwashing is not practiced commercially; depressurization-flushing is the usual method, and in some cases may be the only method used. Sponge-ball cleaning is limited to tubular modules, and has been used successfully in the absence of media filtration (as a feed pretreatment) and any chemical cleaning

(43). Some typical chemical cleaning agents are enzymatic detergents, sodium perborate, sodium tripolyphosphate, triton X-100, formaldehyde, citric acid and urea. Most membrane suppliers specify recommended formulations for chemical cleaning. It has been suggested that small organic molecules, e.g. phenol, alcohol, formamide or methyl acetate that are not normally rejected may be effective for removing colloids from clogged membrane pores (15).

Factors Relevant to Membrane Separation of Fermentation Products

Concentration polarization and fouling contribute significantly to energy consumption and costs of membrane separations. In fact, for desalination by RO, which is actually a particularly favorable process because of the relatively low concentration of rejected salt and the availability of highly selective membranes, energy consumption may be as much as 80% of that required by an efficient evaporative process, such as vapor compression (44). A substantial amount of the initial energy consumed is used to maintain high bulk velocity to the feed across the membrane surface. If the plant is large, with more than 10^6 gal/day capacity, energy recovery would become economically feasible, to reduce membrane system net energy consumption to about 60% (4). However, at the present time, evaporative processes are economically competitive with membranes for desalination, and it does not appear that membrane systems are an obvious first choice for separation of fermentation products. A significant negative factor is the presence of components in fermentation broth that are known to contribute to fouling, e.g., organic fragments, proteins and colloids. Therefore, liquid membranes or pervaporation (which are not critically affected by polarization concentration and fouling) may be more appropriate than RO. Liquid membranes (LM) were first developed in 1968 (45, 46, 47) and may consist of immiscible emulsions in a water or oil phase. The dispersed phase contains an internal reagent which interacts with the product to be separated at the interface between the membrane phase and the internal reagent phase, as indicated by Figure 3. Hydrocarbons (46), phenolics and carboxylic acids (48) have been separated with LM systems, and recovery of carboxylic acids from fermentation with a coupled transport process has been investigated[1]. Pervaporation is a process in which the driving force is from a liquid to a vapor phase across a membrane.

Membranes prepared by grafting vinyl monomers to poly(tetrafluoroethylene) (49) have been studied in applications of pervaporation to ethanol-water. The selectivity values for ethanol, defined as the ratio of alcohol in the product to alcohol in the feed (as volume fractions) were 4 to 5.4 for a poly(tetrafuoroethylene) film grafted with styrene and sulfonated, at alcohol feed concentrations of 30 - 80%.

However, both of these processes tend to be energy intensive: LM because the product may be obtained in a form (e.g. carboxylic acids in an emulsion as sodium salts) that requires additional energy for recovery, and pervaporation because vaporization energy is utilized.

There have also been some recent developments of composite membranes that may be useful for concentration of fermentation products. A composite membrane consists of a very thin film deposited on a porous substrate. Most advanced composite membranes are formed by interfacial polymerization directly on the surface of the substrate (50), e.g. by interfacial polymerization of poly(ethyleneimine) with toluene diisocynate on a polysulphone substrate. The permeabilities of a commercially available composite membrane were determined for more than twenty organic compounds at feed concentrations of 10% or less in Japan (51). Typical rejections were: Ethanol - 97%, isopropanol - 99.5%, n-butanol - 99.4%, glycerine - 99.8%, acetic acid - 86%, propionic acid - 98%,

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[1] Private communication to H. K. Lonsdale from B. R. Smith, Division of Chemical Technology, Commonwealth Scientific and Industrial Research Organization, South Melbourne, Victoria, Australia (Cf. Ref 4).

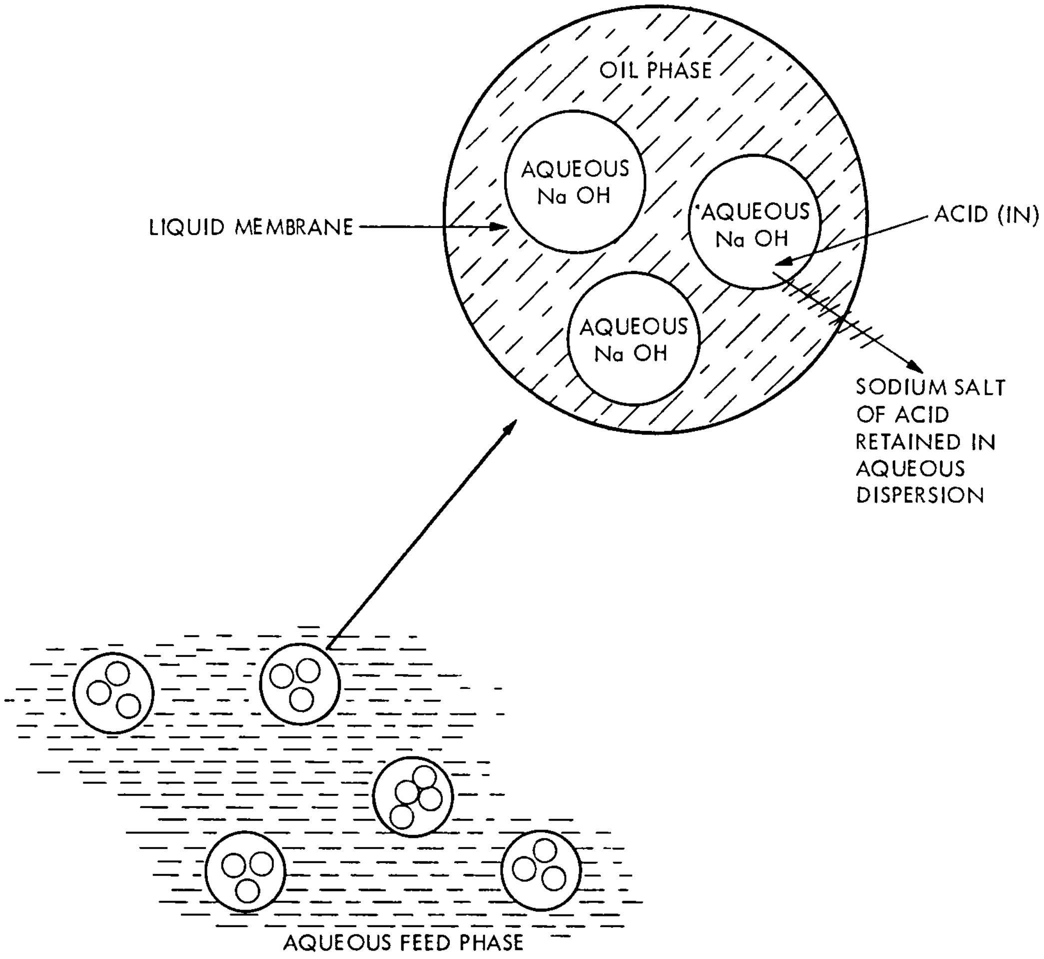

Figure 3. Schematic Diagram of a Liquid Membrane System

and acetone - 97%. Another composite membrane system, which is also commercially available (from Denmark, Cf. reference 37) has also shown decreased permeabilities, e.g. at feed concentrations of 1 - 3%, ethanol permeability was 25% and lactic acid was < 1%. This membrane system is far superior to cellulose acetate membranes because it can be heat sterilized at 80°C, cleaned with dilute (0.5%) nitric acid or alkaline solutions, or disinfected with chlorine. The flux increases with operating temperature by a factor of > 2.5 at 60°C (vs. 20°C operation) and is initially more than three times higher than for a cellulose acetate membrane. This system has been successfully tested with juice from beet and cane, fermentation broth from yeast production, acid hydrolysate from straw, milk and whey, and pulp wastes.

Conclusions

The current status of membrane research and engineering, and potential applications to biocatalyzed processes indicates that advanced membrane systems may lead to substantial improvements in energy efficiency. However, at the present time, it is not clear that membrane separations will be more efficient than alternative processes. In addition to potential concentration polarization and fouling problems, membrane systems are most efficient and selective for concentration of products up to about 40 wt % in water, rather than separation of the product from water. Therefore, the most energy-efficient scenario may be membrane concentration, followed by an alternative process for product isolation, such as a vapor recompression or pervaporation process. In this way, up to about 90% of the water would be removed by the preceding efficient membrane process, e.g., if concentration was increased from 5 to 30%. However, such a process would not be very energy efficient or desirable where the product is more volatile than water, because of the need to separate large amounts of water from small amounts of product.

Although desalination is very different from purification of fermentation products, some important energy-economic relationships mentioned in a recent paper by R. Silver provide an interesting perspective of membrane vs. evaporative processes (52). The minimum thermodynamic energy for desalination is only 2.8 kJ/kg (1.2 Btu/lb). An efficient evaporative process requires about 250 kJ/kg (108 Btu/lb). However, modern desalination plants are combined with steam turbine power plants, so the thermal input for distillation is obtained at an energy cost of 40% at the boiler, or 100 kJ/kg of prime energy. For reverse osmosis, mechanical energy is required and amounts to about 15 kJ/kg. But the fuel (or prime energy) required is three or four times greater, or 45-60 kJ/kg. Therefore, there is a substantial margin for the higher costs of pretreatment, membrane replacement and capital costs of RO. But evaporative systems are still currently competitive, partly because of limited membrane life and fouling problems. Another important factor for some applications is that evaporative processes yield product water that contains less than 50 ppm of salt, while RO water may contain up to 500 ppm.

Since there are many more variables, problems and complexities associated with purification of fermentation products than in desalination of water, it will be necessary to make detailed energy-economic assessments of proposed separation alternatives, followed by an experimental validation effort, to establish the most energy-efficient, economically viable separation technology to be utilized for any specific fermentation process.

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