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Patrick J. Hickey[a][b]; C. Stewart Slater[a]
[a] Chemical Engineering Department, Manhattan College, Riverdale, New York, USA [b] Chem. Eng. Dept., Clemson University, Clemson, SC

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THE SELECTIVE RECOVERY OF ALCOHOLS FROM FERMENTATION BROTHS BY PERVAPORATION

Patrick J. Hickey* and C. Stewart Slater
Chemical Engineering Department
Manhattan College
Riverdale, New York 10471 USA

ABSTRACT

Pervaporation can be successfully utilized to recover various alcohols from fermentation broths and dilute process streams. Hydrophobic membranes, such as silicone-based polymers, have been employed in this application to produce an enriched product. Research in this field has increased dramatically in the past five years and a review of this work is warranted. Fermentations of n-butanol, ethanol, and isopropanol all yielded positive results. The direct integration of a membrane with a bioreactor makes the process more efficient and reduces the effects of product inhibition. A majority of researchers have investigated selective organic permeation from binary aqueous mixtures. These results provide an excellent data base on the permeabilities of alcohols through various membranes. This paper specifically addresses the application of pervaporation to the selective permeation of alcohols from dilute mixtures with particular reference to fermentation broths.

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* - currently at Chem. Eng. Dept., Clemson University, Clemson, SC 29634

INTRODUCTION

Pervaporation (PV) is a membrane separation process that is relatively low on a scale of commercial development maturity as compared to other separation techniques[1], but shows great promise for further growth. The use of pervaporation in the recovery of alcohols from dilute process streams is one area where PV has potential. The focus of this paper is to specifically address the selective permeation of alcohols from fermentation broths and to review the work of researchers in this and associated areas. An overview of process principles and applications is given to acquaint the reader with this technology. We have chosen to discuss a case study describing PV technology integrated into a process scheme to produce fuel grade ethanol from biomass.

Process Principles

Pervaporation selectively separates a liquid feed mixture typically using a non-porous polymeric membrane. The separation is not based on relative volatilities like distillation or evaporation, but is based on the relative rates of permeation through the membrane. The prevailing model for PV is a solution-diffusion mechanism[2], which is common to many membrane processes. The permeating component of the feed goes into solution with the membrane at its surface and then diffuses through the membrane. A vacuum or sweeping gas is applied to the membrane on the permeate side. The permeating component desorbs from the membrane as a vapor and can be collected or released as desired. The chemical potential on both sides of the membrane is the driving force for separation. The permeating component transports through the membrane because its partial pressure on the permeate side is lower than in the saturated vapor. Figure 1 illustrates a basic pervaporation process. Neel[3] describes the various operating modes of pervaporation.

This paper will not review the theory of pervaporation, but will present the basic expressions used to quantify the process. For a thorough presentation of the various aspects of theory and process modeling the reader is referred to other sources[4-11]. The permeability of a component in a mixture can be expressed as a function of diffusivity and solubility in the polymer. Diffusivity

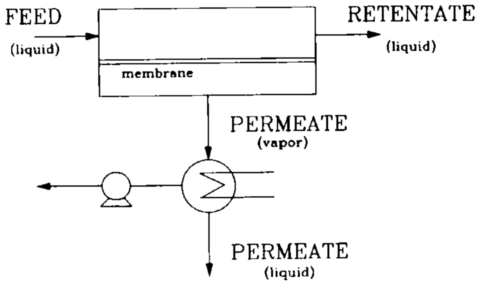

Figure 1. Basic flow diagram of pervaporation.

and solubility are highly dependent on concentration and there is significant interaction between the components of the mixture. Experimental studies are essential in determining separation performance and evaluating process parameters for scale-up and design.

The effectiveness of PV is measured by two parameters, flux and selectivity. Consider the binary mixture of components 'A' and 'B'. The flux is the rate of permeation and can be expressed for the entire permeate or for each component.

J_T = total flux

J_A = flux of component 'A'

J_B = flux of component 'B'

The flux has dimensions of mass/(area x time), [$M/L^2 t$]. Typical units would be $g/cm^2 s$ or $kg/m^2 hr$, etc. The flux can be measured by knowing mass of permeate, membrane area, and time of measurement. The flux can also be defined by the phenomenological expression:

$$J_i = -L_i \frac{\Delta \mu_i}{l} \tag{1}$$

where L_i is the phenomenological coefficient, $\Delta\mu_i$ is the chemical potential driving force across the membrane and l is the membrane thickness.

Selectivity is a measure of the membrane's separation efficiency. It is a ratio of the mass fractions of components 'A' and 'B' for the permeate and the feed.

$$\alpha_B^A = \frac{y_A/y_B}{x_A/x_B} \tag{2}$$

where,
x_A = mass fraction of component 'A' in feed
x_B = mass fraction of component 'B' in feed
y_A = mass fraction of component 'A' in permeate
y_B = mass fraction of component 'B' in permeate

The previous equation is for the selective permeation of component 'A'. A value greater than unity indicates the selective permeation of 'A' over 'B' and a value less than unity results in the selective permeation of 'B' over 'A'. The selectivity is dimensionless and is sometimes described as an enrichment factor, β. The enrichment factor is the ratio of a component's concentration in the permeate to its concentration in the feed.

$$\beta_A = \frac{y_A}{x_A} \tag{3}$$

History

An analysis of pervaporation literature and patents shows that most of the work in this field has been done in the last five years[12]. Figure 2 illustrates the chronology of patents and papers from the early 20th century to 1988. The term "pervaporation" was coined by Kober[13] at the New York State Department of Health's research laboratories in 1917. Binning and associates at the American Oil Company were the first group to undertake a major research effort in pervaporation in the mid 1950s. Binning, Lee, Jennings, and Martin[14] presented a paper on the dehydration of a ternary solution by pervaporation at the 1958 American Chemical Society Meeting. The work of this group in the 1950s and 1960s produced over 10 patents. The publication of papers and the assignment of patents on pervaporation decreased in the late 1960s and early 1970s. Research activity in pervaporation increased in the 1970s due to the energy crises. It was seen as an energy efficient alternative to energy intensive separation operations such as distillation.

The geographic distribution has also been analyzed[12]. This study shows that the majority of research has been done in Japan, Europe, and the United States. Figure 3 illustrates the geographic breakdown of total patents and papers. American researchers who took an early lead in this field now only hold 15 percent of the citations. The first citation noted by Japanese researchers was in 1976, yet they now hold 46 % of the total citations.

Applications

Pervaporation separations have been classified into three types by the authors for convenience in describing the applications of the process. A type 1 separation is the removal of water from an aqueous/organic binary mixture. This area of applications uses water selective hydrophilic membranes to permeate water from the feed mixture. Examples of this are solvent dehydration and dehydration of aqueous solutions at their azeotrope. This type of application has been most commercially developed. Commercial systems using polyvinylalcohol membranes for dehydrating aqueous mixtures (ethanol, isopropanol, acetone, THF, etc.) are now in use[15-18]. A large scale pervaporation unit (150,000 liters per day) used to dehydrate ethanol produced by fermentation was constructed in Betheniville, France[18]. These applications are typically most effective when the concentration of the water to be removed is less than 10 weight percent.

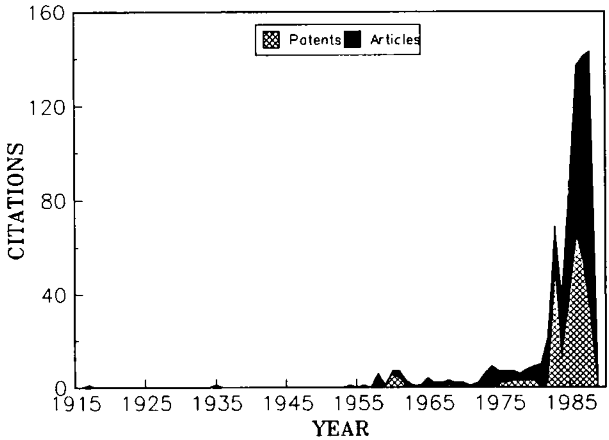

Figure 2. Chronology of Pervaporation Citations - Worldwide

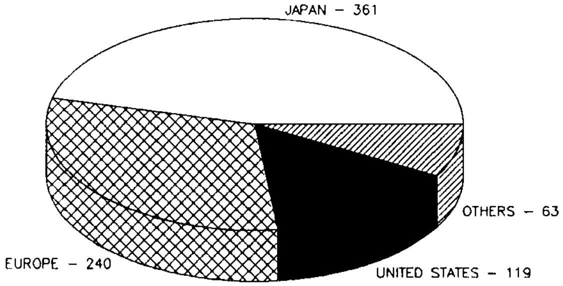

Figure 3. Geographic Distribution of Total Pervaporation Citations

The second general class of pervaporation separations, type 2, is the permeation of organic(s) from an aqueous/organic mixture. These applications use hydrophobic membranes, such as silicone-based polymers, to produce a permeate enriched with organics and a retentate lean of organics. Although the focus of this paper is on the application of PV to selectively permeate alcohol from dilute biochemical processing streams[19-42], applications in solvent recovery, hazardous waste treatment, water purification and beverage processing exists[17]. The removal of trace organic contaminants from groundwaters and industrial effluents has been commercially demonstrated[43,44]. The reduction or removal of ethanol from beer and wine is another successful industrial application of type 2 pervaporation[45].

A type 3 separation involves the permeation of a particular organic from an anhydrous mixture. Examples of separations in this category are aromatics/paraffins, branched hydrocarbons/n-paraffins, olefins/paraffins and isomeric mixtures. This type of separation is not yet commercially viable with the currently available membranes[47-49], although much early research was done in this area[14,46].

The commercial use of pervaporation technology has grown rapidly over the past several years. Pervaporation competes with other traditional separation processes such as distillation, adsorption, extraction, etc. Comparisons between PV and other unit processes should be done on a case by case basis. Some of the more general reasons why PV is preferred are[50]:

1. lower energy/operating costs
2. lower overall system capital costs
3. better separation efficiency (better selectivity and/or flux)
4. pollution-free closed loop operation (no entrainers or additional chemicals needed)
5. easily scaleable for small operations and for plant retrofitting

Case Study

Pervaporation can be utilized to enhance the alcohol fermentation process and to minimize the separation costs. Figure 4 illustrates the way in which PV

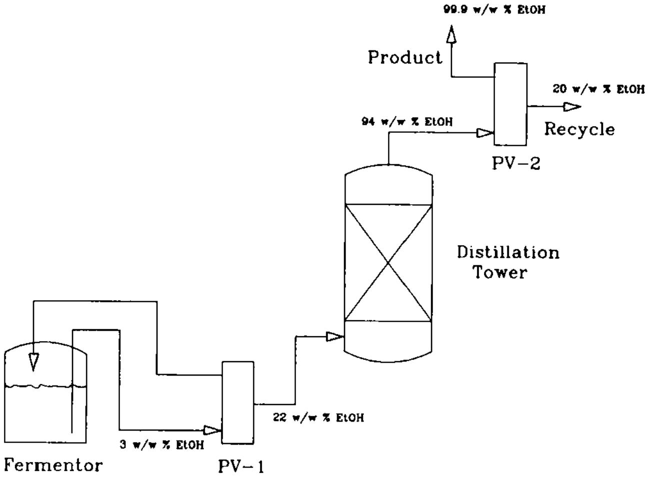

Figure 4. Fermentation-Distillation-Pervaporation Flow Diagram for Ethanol Production.

can be readily integrated into a fermenter-distillation operation. A PV (PV-1) module can be interfaced with a fermenter to form a membrane bioreactor. A PV unit with a hydrophobic membrane not only removes the product but does so at a higher concentration than its natural level. Continuous removal of the product will greatly enhance the fermentation process since product inhibition is reduced. This also concentrates the feed to the distillation column, making the distillation operation more effective. A simple distillation tower is not always capable of a separation due to the nature of azeotropes. Azeotropic distillation may be required to produce the high purities needed in fuel production, creating another separation problem. Azeotropes are not generally a factor in the process, since PV does not separate components on the basis of their different volatilities, although an exception has been noted[51]. A PV (PV-2) unit can be introduced to the middle of the tower to overcome the azeotrope and return the concentrated mixture back to the tower. PV is currently being used to concentrate ethanol beyond its azeotrope concentration (~ 95 wt. % @ 1 atm)[18]. The membrane used is hydrophilic and the mixture is dehydrated producing an ethanol concentration in excess of 99%. In this configuration, the product is that which remains (i.e. the retentate) rather than permeating stream. Pervaporation is more energy efficient than azeotropic distillation. A recent study has indicated that PV used for ethanol dehydration can save ~ 40-70% of the operating costs[52]. In both pervaporation modules (PV-1 and PV-2), the component with the lowest concentration is removed and PV is operated in the most efficient manner.

PV does have some disadvantages. Most membranes are costly, resulting in higher capital expenses. Membrane replacement is expensive as well. Membrane operating problems such as fouling may occur, causing a degradation in flux and selectivity over time. The greatest obstacle to the implementation of PV into the chemical industry is the fear of the unknown. Many plant managers would rather work with a commercially established process than experiment with a technology they know little about.

The fermentation of biomass (e.g. starch, sugar, and cellulose) to alcohol is an established technology with much process development work having been done by the alcoholic beverage industry. The enhancement of this process has greater implications than the production of distilled spirits and commodity chemicals. The application with the greatest potential is the production of alcohol fuels (i.e. ethanol) as an alternative to fossil fuels.

There are several significant reasons that the United States and other industrialized nations have to lessen their reliance on fossil fuels. The fact that there is an exhaustible amount of fossil fuels left in the Earth should be reason enough. The use of gasoline has an harmful effect on the environment, the air quality in many major cities is poor. It is unwise to depend on volatile foreign nations for a large portion of our oil. Currently, the United States imports 46% of its oil (approximately 7.9 million barrels per day)[53]. This reliance will grow as the cost for locating and drilling for oil domestically exceeds the cost of purchasing it on the foreign market. In 1987, the United States imported 44 billion dollars worth of oil, this equates to 29% of the total national trade deficit[53]. The United States has a great surplus of corn, the major raw material in distilling alcohol in this country. The government pays farmers in excess of 5 billion dollars a year to *not* grow corn on 25 to 30 million acres of farmland[54,55]. Many million barrels of oil could be replaced without adding any new corn production from farms. Alcohol fuels have been used as alternative fuels as well as fuel additives. The major advantage of these fuels is that the biomass is a renewable source of energy. Alcohol fuels burn cleaner and can easily be generated domestically. The use of alcohol fuels would boost the agricultural industry, lower the national trade deficit, and lessen the environmental problems caused by our transportation and industrial sectors.

There are several disadvantages to the fermentation process which keep it from being put into large scale use for fuel production. The overwhelming disadvantage to the process is the cost. Fermentation is typically a batch process, usually producing a very dilute product. Fermentation can also be hampered by a phenomena known as product inhibition in which the microbial activity is inhibited with increasing product formation. Alcohols produced from fermentation are usually separated with distillation towers. The distillation process needs fuel to operate its reboilers and is an energy intensive system. A major portion of the cost of producing alcohol from biomass is in removing the product. Therefore, the potential for minimizing the cost of producing fuels from fermentation is in the product recovery stage of the operation.

Ethanol is currently produced in the United States by two processes known as wet-milling and dry-milling[56]. In both processes the corn is fermented, the fermentation broth is distilled, and the distillation overhead is dehydrated. The difference in the processes is in where the by-products are removed. The by-products are removed before the fermentation in wet-milling. In dry-milling the by-products are separated during the distillation process and are then evaporated and sold as "Distillers Dried Grains plus Solubles" or "DDGS". Conventionally in both processes the distillation overhead is dehydrated with azeotropic distillation. Improvements to the dehydration section of the process are already commercialized. The previously mentioned plant in France[18] where type 1 pervaporation is used and the Union Carbide adsorptive heat recovery system[57], which uses molecular sieves to dehydrate ethanol, are examples of this. These dehydration techniques are state-of-the-art and remove the threat of entrainer based pollution and reduce the energy requirement of dehydration.

The proposed process (Figure 4) addresses improving product separation from the fermentation broth, decreasing energy consumption, and improving fermentation kinetics.

Researchers have been investigating the separation of various alcohols from fermentation broths for several years. Two general areas of experimentation have been undertaken. These are the separation of the fermentation product[19-27] and the separation of organics from an aqueous/organic binary system[28-36]. Several other researchers are also mentioned[37-42].

CONTINUOUS SEPARATION FROM FERMENTATION BROTHS

Continuously separating alcohols from a fermentation involves the use of a membrane bioreactor. Research shows that PV is beneficial in reducing the effects of product inhibition in a fermentation. The use of a membrane bioreactor increases glucose consumption and alcohol production. The majority of research with membrane bioreactors has been done in the past few years.

Groot and Luyben[20] studied the separation of n-butanol from a glycose/xylose fermentation broth. n-Butanol broth concentrations decreased when the fermenter was coupled with a PV unit, thus decreasing product inhibition. The conversion of glucose and production of n-butanol increased with decreasing inhibition. A selectivity of 11 was observed at a process temperature of 30°C. The fermenter was more efficient when connected to a pervaporation unit. The yield of product (i.e. mass of product per mass of sugars consumed) was 10 percent greater with continuous recovery. The product yield was 0.30 kg/kg without PV and 0.33 kg/kg with PV.

The recovery of ethanol, n-butanol, and acetone using poly(dimethyl siloxane) (PDMS) membranes was evaluated by Gudernatsch et al[21]. Long term operational problems such as membrane fouling were not found. They stated that PV is a good separation process for fermentation broths since it places no thermal, chemical, or mechanical stress on the fermentation broth. The membrane's flux and selectivity were not found to degrade over a 30 day study. PV is ideal for exothermic fermentation because it removes heat from the system due to the heat of vaporization. The flux of the membrane bioreactor can easily be adjusted by altering the permeate-side pressure. The flux will decrease with increasing pressure. A smaller fermenter may be used since the PV system can be included in the total volume of a bioreactor. Experiments for ethanol permeation proved to be successful. With a downstream pressure of 8 mbar, a total flux of 600 g/m^2·hr was seen for a 5 weight percent feed. Enrichment factors between 5.5 and 6 were also observed at these conditions.

Larrayoz and Puigjaner[22] continuously permeated n-butanol from a fermentation broth using a silicone membrane. Two processes were analyzed, fermentation with PV and without PV. It was found that fermentation without PV required 20 percent more time to completely exhaust the n-butanol in the process. The selectivity decreased from 32.2 to 25.7 and the n-butanol flux increased from 4.42 to 11.05 g/m^2·hr for n-butanol feed concentrations ranging from 1.38 to 1.72 weight percent. The experiments were run at a constant temperature of 37°C. No clear trends were seen for acetone separation. The membrane was as selective for acetone as it was for n-butanol.

Sodeck et al[23] studied the separation of products from a n-butanol/acetone fermentation using a poly(dimethyl siloxane) membrane. Membrane fouling was not observed. This was credited to the non-porous nature of the PV membrane. PV separation was found to be superior to a stripping operation. In addition, product contamination due to microorganism penetration through the membrane did not occur. The fermentation products, n-butanol, acetone, and ethanol, are naturally very dilute, with concentrations less than 1 weight percent. The selectivities for a feed temperature of 41°C were 78, 66, and 9.6 for n-butanol, acetone, and ethanol, respectively. The component permeation rates were 3.44, 1.66, and 0.065 g/m^2·hr, respectively.

Nakao and coworkers[24] extracted ethanol by pervaporation using several membranes. Comparing silicone rubber (SR), polypropylene (PP), and poly(tetrafluoroethylene) (PTFE) membranes, PTFE was found to have the best separation characteristics of flux and selectivity. The PV permeate was found to be 6 to 8 times more concentrated than in the fermentation broth. The membrane bioreactor was superior to straight fermentation in many ways. The best results occurred during low ethanol broth concentration, continuous removal of ethanol, and continuous removal of the broth to remove inorganic salts, non-volatile by-products, and aged cells. A total flux of 3960 g/m^2·hr and a selectivity of 8.9 were observed in experiments using the PTFE membranes at 30°C.

The mass transport of fermentation products was the focus of the research done by Groot et al[25]. The group sought to describe the PV mechanism in several ways and to analyze the transport fundamentals. They took the approach of looking at the solute in the membrane as a dilute solution. A linear trend was seen for binary solutions of water and n-butanol, ethanol, isopropanol, and isoamylalcohol, all between sorption (wt%) and feed concentration up to 1 wt % sorbed. The researchers concluded that when the membrane swelling is low (% sorbed < 1), the diffusion coefficient is constant. Experiments carried out at 30°C and 5 weight percent n-butanol feed produced a selectivity of approximately 60. However, the fluxes found were small. The n-butanol flux increased linearly with increasing n-butanol feed concentration. The water flux decreased slightly with increasing water feed concentration. It was also found that the continuous removal of water by PV from the fermentation increases the productivity.

Groot and coworkers[19,26] examined the continuous fermentation of glucose to n-butanol and isopropanol. Selectivities between 45 and 57 were achieved using silicone tubing in preliminary experiments involving a n-butanol/water binary separation. Experiments using actual fermentations produced selectivities between 20 and 30. This data indicates that the separation of alcohols from fermentations is more complex than in simple binary mixtures for this particular case. It also shows the importance of following up binary work with research on real systems. Glucose conversion was increased by 65-70% with PV. The total productivity of n-butanol and isopropanol, based on mass produced, also increased 70%. No indications of problems with membrane degradation were found in their experiments.

The comparison of a porous polypropylene (PP) membrane to a homogeneous silicone membrane was examined by Kaschemekat et al[27]. They found the PP membrane to produce a greater flux. A process to produce absolute ethanol using a fermenter and two PV units in series is shown. This process requires less energy than traditional distillation or rectification. Experiments showed that the silicone membrane was more effective than a polypropylene membrane. Ethanol permeate concentrations of 33.5 and 25.6 weight percent for silicone and polypropylene, respectively were attained at 30°C and a ethanol feed concentration of 6 weight percent.

SEPARATION OF SIMPLE BINARY MIXTURES

Studies on simple binary mixtures allow a researcher to examine more system variables since it is less complex than a membrane bioreactor. This research is often a precursor to the more involved work with a membrane bioreactor. A researcher can use the binary work to screen potential candidates for the bioreactor work since the binary work is less complicated.

Two basic separations were examined by Changluo and coworkers[28]; the separation of ethanol from a 5 weight percent ethanol binary mixture and the separation of water from azeotropic ethanol/water. The group analyzed several hydrophobic membranes. Symmetric poly(dimethyl siloxane) (PDMS) and composite PDMS with poly(vinyl fluoride) (PVF) membranes were investigated. The composite PDMS/PVF (40 μm) had a separation selectivity of 7 at 20°C for the hydrophobic permeation, as compared to 9 for the homogeneous PDMS (500 μm) at 25°C. The permeate flux for the composite membrane, however, was 28 $g/m^2 \cdot hr$ as compared to 1 $g/m^2 \cdot hr$ for the homogeneous membrane. The low fluxes were probably due to the relatively thick membranes. It would have been difficult to predict the effects of the composite membrane on an actual fermentation separation. This demonstrates why the experimental binary work is important.

Matsumura and Kataoka[29] compared the separation of n-butanol from dilute n-butanol/water binary mixtures using silicone rubber (SR) and oleyl alcohol membranes. The n-butanol concentration in a fermentation never exceeds 0.5 weight percent because n-butanol product inhibition is greater than that of ethanol. Therefore, n-butanol separation is a very good candidate for alternate separation techniques. Both membranes effectively outperformed the vapor-liquid equilibrium curve for n-butanol/water in the dilute range that is applicable for this separation. The SR membrane had a selectivity of 70 and the oleyl alcohol liquid membrane had a selectivity of 180 at 30°C, respectively. The flux of the oleyl alcohol liquid membrane was also higher than that of SR. The separation of acetone from an acetone/water binary was also examined using the oleyl alcohol liquid membrane. The selectivity was found to be 160 at 1 weight percent acetone.

Hennepe and coworkers[30,31] examined the effect of adding zeolites to silicone rubber (SR) membranes. They examined the binary mixtures of water and methanol, ethanol, 1-propanol, and 2-propanol at 25°C with a permeate pressure below 100 Pa. The alcohol flux and selectivity increased as the zeolite concentration (w/w %) increased. The selectivity for ethanol increased from 7 to 39 as zeolite concentration increased from 0 to 70 weight percent. The total flux increased from 175 to 390 $g/m^2 \cdot hr$ over the same range. The water flux was found to be constant. The increase in zeolite concentration from 0 to 70 weight percent affected the selectivity of 1-propanol (from 19 to 50) and the flux of methanol (from 200 to 800 $g/m^2 \cdot hr$) the greatest of all the alcohols tested at 22.5°C.

Separating an ethanol/water binary mixture using two hydrophobic copolymers was investigated by Nagase et al[32]. PDMS was introduced into a poly[1-(trimethylsilyl)-1-propyne] (PTMSP) backbone to make a graft copolymer. PDMS was also made into a graft copolymer with poly(1-phenyl-1-propyne) (PPP). PDMS and PTMSP usually perform close to the vapor liquid equilibrium curve as homogeneous membranes. The homogeneous PPP membrane was found to be selective for water. The polymer's separation ability increases drastically when grafted as copolymers. For the PDMS/PTMSP copolymer, as the PTMSP content of the membrane increased so did the flux and selectivity at 30°C. A maximum was seen at 12 mole percent PDMS at which point the selectivity was 28. For the PPP/PDMS copolymer, flux and selectivity increased with increasing PDMS membrane concentration. A selectivity of 40 was observed for a 7 weight percent ethanol feed at a PDMS concentration of 79 mole percent.

Tanigaki, Yoshikawa, and Eguchi[33,34] have studied the separation of various binary mixtures with several membranes. Their experiments show that a SR membrane transports several pure low molecular weight alcohols to the same degree. These alcohols include methanol, ethanol, 1-propanol, n-butanol, and 1-hexanol. The flux of pure 2-propanol was greater than the other alcohols by a factor of two. The group also studied separations with newly synthesized poly(methyl methacrylate-co-styrene) membranes. The membrane changed from water selective to ethanol selective as the concentration of methyl methacrylate increased. A enrichment factor of 3 and a flux of 5 g/m^2·hr with a 5 weight percent feed were observed using the poly(cyclohexyl methacrylate-co-styrene) membrane at 25 torr and 15°C. A maximum enrichment factor of 5 was seen with a flux of 10 g/m^2·hr at the same conditions with a 25 weight percent feed. The low fluxes can be attributed to the relatively high permeate-side pressure.

Yamada and Nakagawa[35] examined the separation ability of several copolymers composed of both hydrophobic and hydrophilic monomers. The hydrophilic monomers used were N-vinylpyrolidone (NVP), acrylic acid (AA), and 4-vinylpyridine (VP). Methylmethacrylate (MMA), ethylmethacrylate (EMA), and isobutylmethacrylate (IBMA) were the hydrophobic membranes utilized. They separated binary mixtures containing water and methanol, ethanol, 1-propanol, and 2-propanol. Membrane swelling increased with increasing feed alcohol concentration. This shows that the copolymers have a greater affinity for the alcohol over water. The optimum concentration of the copolymer relies greatly on the binary components and the feed concentration. A study examining three copolymers comprised of NVP and each of the three hydrophobic monomers revealed that the enrichment factor increased with increasing hydrophobic monomer concentration. The enrichment factor increased from 1.5 to 18.5 in the case of the NVP-IBMA copolymer, as the IBMA concentration increased from 55 to 90 mole percent.

Slater and coworkers[36] separated an ethanol/water binary mixture at several feed concentrations and process conditions using a poly(dimethyl siloxane) membrane. Several trends were observed. The total and ethanol fluxes increased for a 5 weight percent ethanol feed and 1 torr permeate pressure with increasing temperature in an Arrhenius-like manner. A selectivity of 9 was found between the temperatures of 20 and 90°C with minor variation. The total and ethanol flux decreased with increasing permeate side pressure for a 5 weight percent ethanol feed at 30°C. The effects of feed concentration on the flux and selectivity were observed using a 30°C feed with a permeate side pressure of 1 torr. The total flux increased from 102 to 1115 $g/m^2 \cdot hr$ as the feed concentration increased from 0 to 100 weight percent. The membrane's selectivity decreased from 11 to 1 as the ethanol feed concentration increased from 1 to 100 weight percent.

Other researchers have examined many additional separations with various polymer materials. Lee and Belfort[37] studied the separation of ethanol and chloroform aqueous binary mixtures with a variety of membranes including poly(vinyldimethylsiloxane) (PVDMS) and poly(vinylidenefluoride) (PVDF). Copolymers of tetrafluoroethylene (TFE) and alkyl vinyl ethers were utilized by Nakamura and coworkers[38] to separate ethanol/water binary mixtures. Lorenz et al[39] discuss the use of pervaporation as a sampling device. Pervaporation is used as an on-line detector in fermentation broths. The organic concentration in the broth can be determined by measuring the organic concentration in the permeate. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) was found to preferentially permeate ethanol over water by Masuda et al[40] and Ishihara et al[41]. Masouka and coworkers[42] separated ethanol from an ethanol/water binary mixture using plasma-polymerized membranes consisting of hexafluoroethane and allylamine.

SUMMARY

Pervaporation is an effective membrane-based separation technique for a variety of process streams. It is useful in separating organics from dilute mixtures and can be incorporated into the areas of hazardous waste treatment, biochemical processing, water purification, and beverage processing. Pervaporation can also be applied to the recovery of the products of fermentation, particularly alcohols. It is effective because the low concentrations of alcohol that exist in the broth can be selectively permeated through hydrophobic membranes. Membranes composed of polymers such as poly(dimethyl siloxane), poly(tetra fluoroethylene) and poly[1-(trimethylsilyl)-1-propyne] have been successfully employed in separation studies. The use of pervaporation coupled to a fermenter not only acts as a means of separation, but also as a production enhancer by reducing product inhibition. One of the most important uses of pervaporation is in the production of alcohol fuels since the separation stage of the process shows the greatest potential for cost savings.

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NOMENCLATURE

J_A - flux of component 'A' [g/m$^{2}\cdot$hr]
J_B - flux of component 'B' [g/m$^{2}\cdot$hr]
J_T - total flux [g/m$^{2}\cdot$hr]
J_i - flux of single component 'i' [g/m$^{2}\cdot$hr]
x_A - mass fraction of component 'A' in feed
x_B - mass fraction of component 'B' in feed
y_A - mass fraction of component 'A' in permeate
y_B - mass fraction of component 'B' in permeate
α_B^A - selectivity [dimensionless]
β - enrichment factor [dimensionless]
ℓ - membrane thickness [m]
L_i - phenomenological coefficient [g/m$\cdot$hr]
$\Delta\mu_i$ - chemical potential difference across membrane [J/kg]

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