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Mandy Wood[a]; Takeshi Matsuura[a]; Z. Duvnjak[a]
[a] INDUSTRIAL MEMBRANE RESEARCH INSTITUTE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF OTTAWA, OTTAWA, ONTARIO, CANADA

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Effect of the Addition of Fructose on the Pervaporation of Ethanol/Water Mixtures by Silicone-Rubber-Coated Polyethersulfone Membranes

MANDY WOOD, TAKESHI MATSUURA, and Z. DUVNJAK
INDUSTRIAL MEMBRANE RESEARCH INSTITUTE
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF OTTAWA
OTTAWA, ONTARIO K1N 6N5, CANADA

ABSTRACT

Composite hollow fiber membranes were prepared by coating polyethersulfone hollow fibers with silicone rubber. The hollow fiber membranes so produced were found to be water selective when they were used for the separation of feed ethanol/water mixtures by pervaporation. When fructose was added to feed ethanol/water mixtures, a decrease in permeation rate and an increase in water selectivity were observed. The decrease in the permeation rate was possible to assume, but the noticed increase in water selectivity was against our expectation, since the vapor pressure of water decreases while that of ethanol increases when sugars are added to mixtures of ethanol and water. Water selectivity of the membrane was enhanced with an increase in the amount of fructose in the feed.

INTRODUCTION

Fructose is widely used in the food and beverage industries because it is the sweetest naturally occurring carbohydrate and has other advantages over conventional sweeteners (1).

Sugar syrups containing 42% fructose, 50% glucose, and 8% other saccharides are manufactured by isomerization of glucose obtained from corn starch (2). The fructose content of these syrups is limited by the equilibrium of the isomerization reaction. To produce a syrup more enriched with fructose requires separation of glucose and fructose.

The separation of glucose and fructose is difficult. It can be carried out chromatographically, but this method is expensive (3). An alternative is to convert the glucose to a substance more easily separated from fructose. It has been reported that glucose from a glucose–fructose mixture can be selectively converted to biomass by *Tricholoma nudum* (4), or to ethanol by *Fusarium* sp. F5, *Mucor* sp. M 105 (5), *Zymomonas mobilis* (6–8), or by *Saccharomyces cerevisiae* ATCC 36859 (9), while fructose is partially consumed or is not consumed at all. Ethanol and biomass can then be separated from the solution by distillation or filtration, respectively.

Membrane separation is an alternative which would allow the bioreaction and separation to be performed simultaneously. Removal of ethanol as it is being formed is desirable because ethanol has a toxic effect on the microbial cells and causes inhibition of the fermentation reaction.

The objective of this work is to study the effectiveness of pervaporation using silicone-rubber-coated polyethersulfone hollow fibers as a means of separating ethanol from mixtures of a saccharide, ethanol, and water. This study is considered as the preliminary step to our final goal of constructing a bioreactor relevant to the fermentation process mentioned above.

Hollow fibers were chosen because they offer high surface area to volume ratios and also are able to withstand the transmembrane pressure difference without extra support. Porous polyethersulfone hollow fibers were prepared, and the surface was coated on the shell side with a single or double layers of silicone rubber. The above system was chosen since polyethersulfone is easily manufactured into hollow fibers with the desired pore size and porosity, and it is insoluble in the solvent used in the coating procedure (10). Despite the initial intention to prepare ethanol-selective hollow fibers, the hollow fibers so produced were water selective in pervaporation of aqueous ethanol solution. Interestingly, however, an increase in water selectivity was observed when either glucose or fructose was added into the feed aqueous ethanol solution. Since this observation is quite unexpected in view of the vapor pressure change of ethanol and water occurring in the presence of saccharides, the experimental procedures and the pervaporation results are reported in detail.

EXPERIMENTAL

Materials

Polyethersulfone (PES) was Victrex 200P supplied by Imperial Chemical Industries. Polyvinylpyrrolidone (PVP) of molecular weight 10,000 was used as a nonsolvent additive. The polymer powder was dried at 150°C for 4 hours before use. Silicone rubber used for surface coating was Sylgard 184 elastomer from Dow Corning, *N*-Methyl-2-pyrrolidone (NMP) and hexane were supplied by J. T. Baker Chemical Co.

Membrane Preparation

The hollow fibers were spun from a spinning dope of 22 wt% PES and 17.6 wt% PVP in NMP solvent under the following spinning conditions:

Pressure applied for the extrusion of polymer solution: 138 kPag
Temperature of the spinning dope: 60°C
Internal coagulant bath: water at 25°C
External coagulant bath: water at 5°C
Air gap: 60 cm
Flow rate of internal coagulant: 6.0 mL/s

The details of the equipment used for the hollow fiber spinning are described elsewhere (11).

Design of the Hollow Fiber Module

A schematic diagram of the hollow fiber module is given in Fig. 1. Nineteen hollow fibers were installed inside a Plexiglas shell and sealed in place at either end using Devcon 5 minute epoxy resin. The end of the hollow fibers was open to a common area separated from the rest of the shell by an O-ring. A tube passing from this area would allow a vacuum to be applied to the bores of the hollow fibers.

The Plexiglas shell of the module was fitted with two port holes for recycle of feed solution. A hole on the top of the module was fitted with

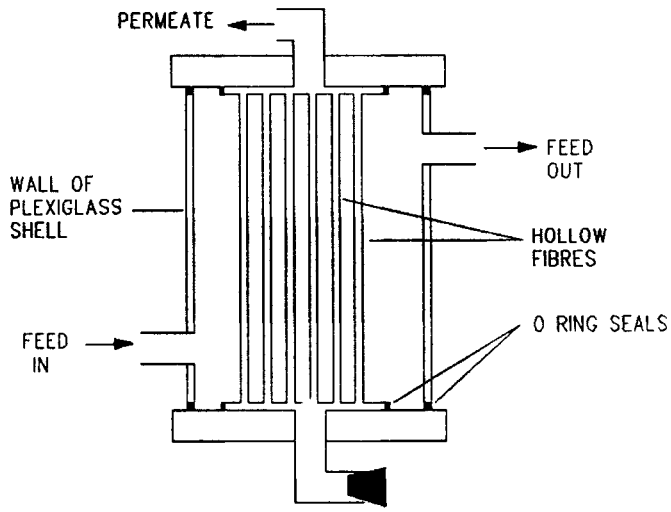

FIG. 1 Schematic diagram of hollow fiber module.

a syringe to allow easy removal of any air trapped in the top of the module when it was filled with feed solution.

The length of each individual hollow fiber was 14.5 cm. The overall surface area was 125.5 cm^2.

Coating of Hollow Fibers

A silicone rubber solution was prepared by dissolving 60 g Sylgard 184 elastomer and 18 g Sylgard 184 curing agent in 222 g hexane. The shell of the hollow fiber module was filled with the solution, ensuring each hollow fiber was completely bathed with the solution. The module was then left for 30 minutes; it was noted that the hollow fibers became very swollen during this period. The solution was drained from the module. The module was then left open to air for 90 hours for the hexane solvent to evaporate. Air was slowly passed through the module for a further 27 hours to complete the drying. The coating is estimated to be 4 μm thick.

Pervaporation

The schematic of the apparatus used in the pervaporation experiments is shown in Fig. 2. The feed solution is recycled through the shell side of the hollow fiber module by a recycle pump at a flow rate of 286 mL/min. The bore side of the hollow fiber is connected to a cold trap cooled with

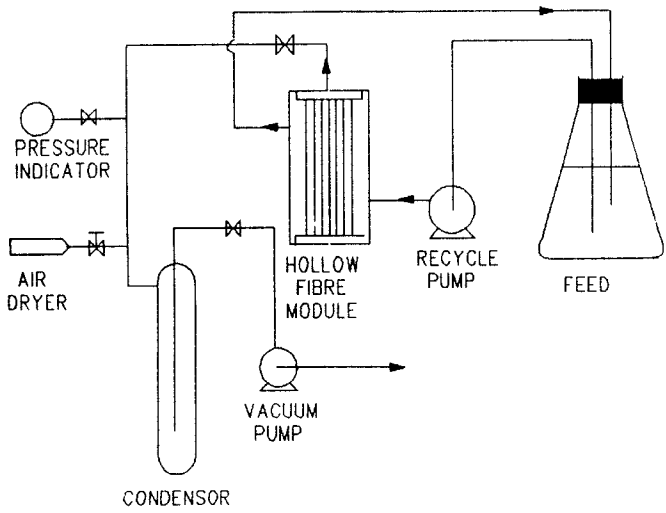

FIG. 2 Schematic diagram of apparatus used in pervaporation experiments.

liquid nitrogen, which is followed by a Duo-Seal vacuum pump. When vacuum is applied, the permeant permeates through the hollow fiber wall from the shell to the bore side and is collected in the cold trap. Each pervaporation experiment lasted for 1 hour, and the permeant collected in the cold trap during the run was weighed to determine the permeation rate. The feed and permeate samples were subjected to analysis for ethanol by gas chromatograph (Varian 3400 with a CHROM 102 column) and for glucose and fructose by liquid chromatograph (Waters with a Polypore CA column).

After steady state was established, two runs were carried out under the same experimental conditions and the results were considered.

RESULTS AND DISCUSSION

Table 1 shows the results of pervaporation experiments on pure water and aqueous glucose solutions. The flux of pure water was 8.00×10^{-5} kg/m^2·s. When the glucose concentration was 5.0 wt%, the flux decreased to 5.61×10^{-5} kg/m^2·s. Further increasing its concentration in the feed had little effect on the flux. No glucose was detected in the permeate.

Table 2 shows results for the pervaporation of 5 wt% ethanol solution and the effect of adding 5 wt% fructose to the feed. Pervaporation of the 5 wt% ethanol solution gave a permeation flux of 10.61×10^{-5} kg/m^2·s, which is almost one-third higher than for water alone (Table 1). The ethanol concentration in the permeate was less than in the feed, indicating the hollow fiber was water selective. The separation factor, α, for 5 wt% ethanol solution was 1.36. The separation factor was defined as

$$\alpha = \frac{\text{weight fraction of water in permeate/ weight fraction of water in feed}}{\text{weight fraction of ethanol in permeate/ weight fraction of ethanol in feed}}$$

TABLE 1
Permeation Flux for Pervaporation of Water and Glucose Solutions Using Hollow Fibers with Single Silicone Rubber Coating

Run	Water in feed (wt%)	Glucose in feed (wt%)	Permeation flux $\times 10^5$ (kg/m^2·s)	Water in permeate (wt%)	Glucose in permeate (wt%)
1	100.0	0	8.00	100.0	0
2	95.0	5.0	5.61	100.0	0
3	90.0	10.0	6.08	100.0	0
4	85.0	15.0	5.58	100.0	0

TABLE 2
Flux and Separation Data for the Pervaporation of Ethanol Solutions and the Effect of Adding Fructose, Using Hollow Fibers with Single Silicone Rubber Coating

Run	Ethanol in feed (wt%)	Fructose in feed (wt%)	Total permeate flux × 10^5 (kg/m^2·s)	Ethanol flux in permeate × 10^5 (kg/m^2·s)	Water flux in permeate × 10^5 (kg/m^2·s)	α
5	4.9	0	10.75	0.39	10.36	1.44
6	5.0	0	10.61	0.42	10.19	1.36
7	4.7	5.15	5.55	0.067	5.50	4.33

where weight fraction of water is [wt% of water/(wt% of water + wt% of ethanol)]. Similarly, weight fraction of ethanol is [wt% of ethanol/(wt% of water + wt% of ethanol)].

Despite our initial intention to prepare an ethanol-selective membrane by coating the surface of porous polyethersulfone hollow fibers with hydrophobic silicone rubber, the hollow fiber was water selective.

This result can be understood by considering the contribution of the bottom polyethersulfone layer and the top silicone rubber layer to the overall resistance of the bilayer membrane against the flow of the permeant. When the polyethersulfone layer is thick and less porous, while the silicone rubber layer is thin, the former layer contributes more to the overall resistance and governs the selectivity. Since the polyethersulfone layer is water selective because of its hydrophilic nature, the bilayer membrane becomes water selective. On the other hand, when the polyethersulfone layer is thin and very porous, while the silicone rubber layer is thick, the bilayer membrane becomes selective to organic solutes (12). Obviously, the polyethersulfone hollow fibers we made were not porous enough to render the bilayer membrane ethanol selective.

Table 2 also indicates that the presence of 5.15 wt% fructose in the feed solution caused the separation factor to increase to 4.33. Water flux was slightly higher than one-half, whereas the ethanol flux was one-sixth, of the value obtained in the absence of fructose. As a result, the membrane became more water selective.

This is rather surprising when the vapor pressure data are considered. Table 3 includes partial vapor pressures of ethanol and water with and without sucrose in the solution (13). The table indicates that the partial vapor pressure of ethanol increases whereas that of water decreases when sucrose is added to the solution. Similar data are expected with fructose, or glucose, in the ethanol solution. Consequently, we would expect a

TABLE 3
Partial Vapor Pressure Data Pertinent to Ethanol/Water/Sucrose Mixture[a]

Concentration of sucrose (mol/L)	Vapor pressure of ethanol (mmHg)	Vapor pressure of water (mmHg)
0.0	20.2	17.2
0.072	21.3	14.6

[a] Data obtained from Reference 13 for a solution of 38 wt% ethanol in water.

decrease in water flux and an increase in ethanol flux when fructose, or glucose, is dissolved in the feed solution, since the transmembrane activity difference is the driving force for the transport of the permeant. It was indeed the case for reverse osmosis experiments. As de Pinho et al. have reported, ethanol was more concentrated in the permeate when glucose was added to the feed (14).

The pervaporation data shown in Table 2 are, however, against the above expectation. These findings are in agreement with those obtained by Heisler et al. who studied the pervaporation of aqueous ethanol solution using cellophane membranes (15). They found adding glucose increased the water content of the permeate from 65 to 81% when the feed ethanol concentration was 50 wt%. Addition of sodium chloride and sodium citrate caused an even greater increase in the water content of the permeate. The difference between Heisler et al.'s and our experiments is the membrane. Although both groups used water-selective membranes, Heisler et al.'s was hydrophilic cellophane membranes whereas the surface layer of the hollow fiber membranes used in this work was coated with hydrophobic silicone rubber. At present, it is difficult to identify the cause of the increase in water selectivity. As mentioned earlier, the transmembrane activity difference of each permeant cannot explain the experimental results. Probably, water molecules can readily pass through the membrane whereas the passage of ethanol molecules through the membrane is more restricted when carbohydrate molecules are trapped in the membrane, as postulated by Heisler et al. (15).

Table 4 shows the effect of fructose concentration on the flux and selectivity of the membrane when ethanol concentration was kept in the 8.3 to 8.5 wt% range. Apparently, the total flux decreased and the separation factor increased with an increase in fructose concentration.

Table 5 shows the effect of ethanol concentration on the flux and selectivity of the membrane when 5 wt% fructose was present in the feed solution. The separation factor increased with an increase in the ethanol concentration until the latter concentration reached 8.5 wt%. The hollow

TABLE 4
The Effects of Increasing the Fructose Content of the Feed on the Pervaporation of an 8.5% Ethanol Solution, Using Hollow Fibers with a Single Silicone Rubber Coating

Run	Ethanol in feed (wt%)	Fructose in feed (wt%)	Total permeate flux × 10^5 (kg/m^2·s)	Ethanol flux in permeate × 10^5 (kg/m^2·s)	Water flux in permeate × 10^5 (kg/m^2·s)	α
8	8.5	4.85	6.39	0.108	6.28	5.72
9	8.3	6.75	5.58	0.081	5.50	6.49
10	8.3	9.00	5.53	0.069	5.47	7.92

fibers were visibly swollen in the ethanol solution and the degree of swelling appeared to increase with an increase in the ethanol concentration, which is reflected by the increase in the flux of both permeates. When the ethanol concentration reached 15.3 wt%, the hollow fiber was highly swollen and a remarkable increase in the flux was observed. The separation factor decreased to 3.94. The change of the membrane was irreversible. When the membrane was further tested for pervaporation performance with 9.0 wt% ethanol solution without fructose, the total flux was 29.4 × 10^{-5} kg/m^2·s with practically no selectivity between water and ethanol. The hollow fibers were therefore coated with another layer of silicone rubber before being used for pervaporation experiments. These hollow fibers are called hollow fibers with two layers of silicone rubber coating hereafter.

Hollow fibers with two layers of silicone rubber coating were tested for their performance, and the results listed in Tables 6 and 7. When the

TABLE 5
The Effects of Increasing the Ethanol Content of the Feed on the Pervaporation of a 5% Fructose Solution, Using Hollow Fibers with Single Silicone Rubber Coating

Run	Ethanol in feed (wt%)	Fructose in feed (wt%)	Total permeate flux × 10^5 (kg/m^2·s)	Ethanol flux in permeate × 10^5 (kg/m^2·s)	Water flux in permeate × 10^5 (kg/m^2·s)	α
7	4.7	5.15	5.56	0.067	5.50	4.33
11	6.7	5.15	5.81	0.089	5.72	5.07
8	8.5	4.85	6.39	0.108	6.28	5.72
12	15.3	5.00	8.39	0.390	8.00	3.94

TABLE 6
Flux and Separation Data for the Pervaporation of Ethanol Solutions and the Effect of Adding Fructose, Using Hollow Fibers with Two Silicone Rubber Coatings

Run	Ethanol in feed (wt%)	Fructose in feed (wt%)	Total permeate flux × 10^5 (kg/m^2·s)	Ethanol flux in permeate × 10^5 (kg/m^2·s)	Water flux in permeate × 10^5 (kg/m^2·s)	α
13	5.2	0.0	4.56	0.10	4.44	2.49
14	9.0	0.0	4.58	0.178	4.42	2.48
15	5.1	5.0	3.47	0.064	3.42	3.14

results of Run 13 in Table 6 are compared with those of Runs 5 and 6 in Table 2, we notice that the total permeation rate of two coatings was less than one-half of that for a single coating. The selectivity for water, on the other hand, was greater when two coatings were applied. This means that the decrease in the membrane flux with an increase in the number of coating is not necessarily because of the thicker silicone rubber layer. The porous polyethersulfone support layer could also be affected during the second coating of silicone rubber. Table 6 also indicates that the flux decreased and the selectivity increased in the presence of fructose in the feed solution. Interestingly, the gain in the selectivity was not as much as in the case of the single coating. Table 7 shows the effect of an increase in the ethanol concentration while the feed fructose concentration was maintained at 5 wt%. The data in Table 7 are parallel to those in Table 5. The selectivity showed a maximum while the total permeation rate kept increasing with an increase in the feed ethanol concentration. The

TABLE 7
The Effects of Increasing the Ethanol Content of the Feed on the Pervaporation of a 5% Fructose Solution, Using Hollow Fibers with Two Silicone Rubber Coatings

Run	Ethanol in feed (wt%)	Fructose in feed (wt%)	Total permeate flux × 10^5 (kg/m^2·s)	Ethanol flux in permeate × 10^5 (kg/m^2·s)	Water flux in permeate × 10^5 (kg/m^2·s)	α
15	5.1	5.0	3.47	0.064	3.42	3.14
16	7.4	5.0	3.56	0.081	3.42	3.57
17	8.5	5.1	3.67	0.106	3.56	3.36

membrane changed irreversibly after Run 17, with a significant increase in the flux and a decrease in the selectivity.

CONCLUSIONS

The following conclusions can be drawn from the experimental results stated above.

1. It is possible to prepare water-selective polyethersulfone hollow fiber membranes in pervaporation of an aqueous ethanol solution by coating the shell-side surface of the hollow fiber with a single or double layer of silicone rubber.
2. The composite membrane becomes even more water selective in pervaporation of an aqueous ethanol solution when the aqueous ethanol feed solution contains fructose. The selectivity toward water is intensified with an increase in the fructose concentration in the feed.
3. With such composite membranes, pervaporation of an aqueous glucose or fructose solution and pervaporation of an aqueous ethanol solution containing glucose generate a permeate containing no sugar. The permeate flux of the composite membrane is lower with sugar in the feed than without it.
4. The selectivity toward water also increases with an increase in ethanol concentration until a point is reached where an irreversible change occurs with the membrane due to excessive swelling. The permeate flux, on the other hand, keeps increasing with an increase in ethanol concentration.

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