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Effect of Protein on Flux and Selectivity in Pervaporation of Ethanol from a Dilute Solution

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ABSTRACT

The separation of ethanol from a 2% w/w ethanol–water mixture by pervaporation through a thin polydimethyl-siloxane (PDMS) membrane sheet was studied with and without a dissolved vegetable protein in the feed solution. Total flux and ethanol selectivity were measured at different feed temperatures (40, 50, and 60°C) and permeate-side pressures (1, 10, 20, and 40 mm Hg). An analysis of variance was done to detect effects and interactions. Protein at 10 g/L did not foul the membrane under the conditions used and had no significant effect on flux or selectivity. The effects of protein and temperature on ethanol selectivity interacted slightly.

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Key Words: Pervaporation; Ethanol–water mixture; Flux; Selectivity; Protein.

INTRODUCTION

Ethanol from lignocellulosic biomass fermentation is receiving increased attention as an alternative renewable biofuel and gasoline extender, both for environmental and economic reasons. Although ethanol has long been a valuable starting material in the petrochemical and pharmaceutical industries, increasing pressure to use it to improve petroleum-combustion efficiency has made corn-based production justifiable. However, limitations on the availability of corn and the environmental burden represented by the nitrogen-fertilizer requirements of corn production, have led to examine lignocellulosic materials as an alternative starting material for ethanol production. Forage has shown interesting potential for ethanol production.[1–4] Analysis of different forages indicates that they contain up to 61% carbohydrate material (33% cellulose and 28% hemicelluloses), 10% crude protein, 5% lignin, 2% lipids, 8% ash, and 14% other materials.[5] Cellulose and hemicelluloses are convertible into glucose and xylose by acid and enzymatic hydrolysis. The sugars may be fermented to ethanol by yeasts. Mes-Hartree et al[6] found that the maximum level of solids in an optimized enzymatic hydrolysis is not greater than 10% w/v. Belkacemi et al[1] found that at 10% solids, the maximum efficiency of enzymatic saccharification was 80%, while conversion to ethanol by yeast fermentation reached 54% of the theoretical yield. Fermentation broth supernatants thus obtained contain about 2% w/w ethanol, 2.5 and 4.5 g/L residual glucose and xylose, about 10 g/L soluble protein, and small quantities of organic acids and soluble lignin. Since distillation is not practical with ethanol solutions of such low concentration, pervaporation has been considered as a means of recovering ethanol from these fermentation broths. In pervaporation, variations in feed-solution temperature and permeate-side pressure affect liquid flux through the membrane, as well as membrane ethanol selectivity. The presence of residual sugar and protein may also be expected to affect membrane flux and ethanol selectivity. We previously investigated the effect of residual sugars on flux and ethanol selectivity.[7] Due to the solubility of proteins in fermentation broth, they should affect thermodynamic properties, such as ethanol and water vapor pressures, and, therefore, flux and ethanol selectivity. Proteins may also foul membrane pores (in the case of porous membranes) or form a polarization layer on the membrane surface, particularly in laminar flow conditions, and increase the mass-transfer resistance to permeation. In either case, membrane characteristics, flux, and

ethanol selectivity will be affected. The main objective of this work was to study the effect of plant protein at a concentration of 10 g/L on flux and ethanol selectivity at different feed temperatures and permeate-side pressures during pervaporation of 2% w/w ethanol solution. These protein and ethanol concentrations are typical of those obtained in the supernatant of enzyme-hydrolyzed forage fermented by yeast.[1]

MATERIALS AND METHODS

Experimental Setup

The pervaporation equipment has been previously described in Aroujalian et al.[8] A 2% w/w ethanol–water solution containing 10 g/L of isolated soy protein (PRO FAM 974, Archer Daniels Midland Co., Decatur, IL, USA) was pumped from a reservoir to the shell side of a 10-μm polydimethyl-siloxane (PDMS) film membrane (KGSS Research Institute, Geesthacht, Germany). The effective surface area of the membrane was 100 cm^2. The feed solution was pumped at a volumetric flow rate giving a Reynolds number of 1000. The permeate was weighed and permeate–ethanol concentration was measured as previously described.[8] Selectivity and flux were calculated by the following equations:

$$\alpha_{EtOH} = \frac{(y_i/y_j)}{(x_i/x_j)} \tag{1}$$

$$Flux_{Total} = \frac{Q}{S \cdot t} \tag{2}$$

where y_i and y_j are permeate-side ethanol and water-mass fractions; x_i and x_j are feed-side ethanol and water-mass fractions; and Q, t, and S refer to permeate-quantity, time-interval, and effective-membrane surface area, respectively. Flux and ethanol selectivity at permeate-side pressures of 1, 10, 20, and 40 mm Hg and feed temperatures of 40, 50, and 60°C were determined. Data were analyzed by Fisher's test (ANOVA) at the 5% level of confidence using SAS statistical software. The experimental plans were factorial 2 × 4 (two-protein concentration at levels of 0 and 10 g/L and four permeate-side pressure levels of 0, 10, 20, and 40 mm Hg) and factorial 2 × 3 (two-protein concentration at levels of 0 and 10 g/L and three feed-temperature levels of 40, 50, and 60°C) with three repetitions for each combination of treatments.

RESULTS AND DISCUSSION

Time Dependency on Permeation

The precipitation of protein on the membrane surface, as well as membrane-fouling phenomenon, was studied first by measuring total flux vs pervaporation time. As shown in Fig. 1, steady-state permeation was reached early, and no significant difference was observed for total flux and ethanol selectivity with and without protein. This experiment showed that at least for a Reynolds number of 1000, no protein precipitation on the membrane surface

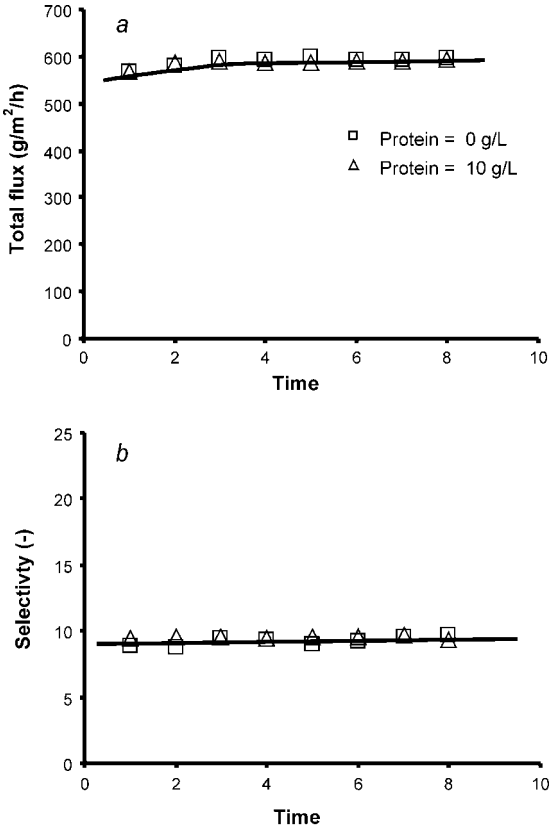

Figure 1. Time dependency of total flux (a) and ethanol selectivity (b) with and without protein in solution ($C_0 = 2\%$ w/w ethanol, $P_2 = 1$ mm Hg, Re = 1000).

occurred. The lack of protein precipitation on the membrane surface is likely due to the nonporous nature of the membrane and the high smoothness of its surface.

Effect of Permeate-Side Pressure

Total flux and ethanol selectivity vs permeate-side pressures with and without protein are plotted in Fig. 2. No significant difference was observed for total flux and ethanol selectivity curves between feed solutions with and

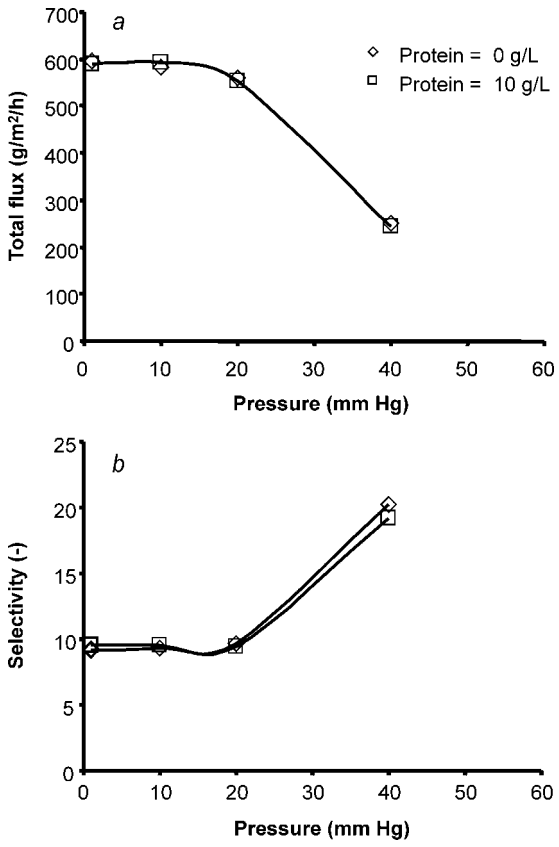

Figure 2. Effect of permeate-side pressure on total flux (a) and ethanol selectivity (b) with and without protein in solution ($T = 60°C$, $C_0 = 2\%$ w/w ethanol, $Re = 1000$).

without protein, except for a small variation (5.3%) in ethanol selectivity at a permeate-side pressure of 40 mm Hg. As shown in Fig. 2a, there was a slight linear decrease in total flux over permeate-side pressures of 1 to 20 mm Hg, while a large drop was observed at a permeate-side pressure of 40 mm Hg for two curves. The variation in total flux vs permeate-side pressure was generally similar to that of solutions with and without protein. Ethanol selectivity did not change with permeate-side pressures up to 20 mm Hg at either 0 or 10 g/L protein in the feed solution, but a large variation was observed with the permeate-side pressure at 40 mm Hg (see Fig. 2b). Thus permeate-side pressure had no effect on the flux curves, although a slight effect was observed on ethanol selectivity curves. Analysis of variance confirmed these findings, and neither protein concentration nor its interaction with permeate-side pressure had a significant effect on total flux and ethanol selectivity (Table 1).

Effect of Feed Temperature

Total flux and ethanol selectivity vs feed temperatures with and without protein in the solution are plotted in Fig. 3. As shown in Fig. 3a, an increase in total flux was observed as feed temperature increased. Since the feed solution

Table 1. Analysis of variance for total flux and ethanol selectivity vs. permeate-side pressures (effect of protein).

Source of variance	Degree of freedom	Sum of squares	Mean squares	Computed *F*	Probability
Total flux					
Repetition	2	168	84	0.37	0.6966
Protein (Pr)	1	38	38	0.17	0.6874
Pressure (P)	3	500,164	166,721	736	0.0001
Pr*P	3	350	117	0.51	0.6792
Error	14	3173	227	—	—
Ethanol selectivity					
Repetition	2	1.04	0.52	1.07	0.3685
Protein (Pr)	1	0.26	0.26	0.55	0.4725
Pressure (P)	3	472	157	324	0.0001
Pr*P	3	1.79	0.60	1.23	0.3351
Error	14	6.80	0.48	—	—

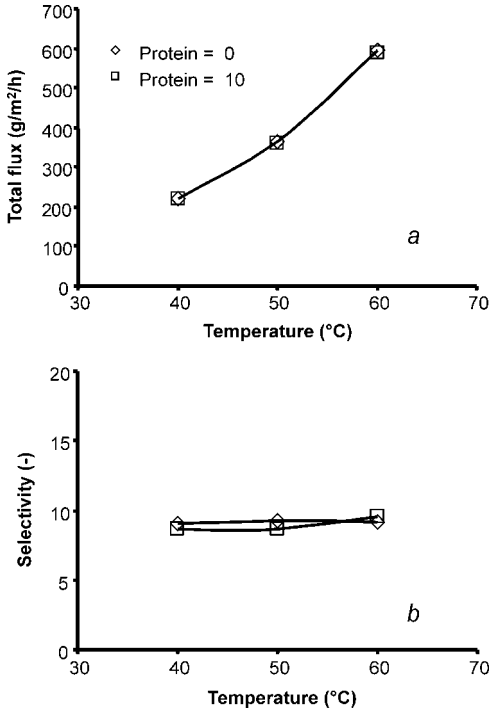

Figure 3. Effect of feed temperature on total flux (a), ethanol selectivity (b) with and without protein in solution (P = 1 mm Hg, C_0 = 2% w/w ethanol, Re = 1000).

was in direct contact with the membrane, higher solution temperature meant higher membrane temperature, increasing the segmental motion of membrane-polymer chains and resulting in greater membrane-free volume and increased passage of permeants through the more open structure. No significant difference was observed between 0 and 10 g/L solution protein concentration, however. The effect of protein on ethanol selectivity vs feed temperatures is plotted in Fig. 3b. The effect appears to be negligible, since only a very slight difference between the curves is apparent. There is, however, a statistically significant interaction between protein and temperature (Table 2). The selectivity at 60°C appears to increase slightly in the presence of protein. Temperature effects are to be expected when dissolved proteins are involved, since protein solubility may decrease quickly beyond a critical temperature.

Table 2. Analysis of variance for total flux and ethanol selectivity vs. feed temperature (effect of protein).

Source of variance	Degree of freedom	Sum of square	Mean squares	Computed *F*	Probability
Total flux					
Repetition	2	40	20	0.93	0.4261
Protein (Pr)	1	93	93	4.39	0.0626
Temperature (T)	2	420,950	210,475	9893	0.0001
Pr*T	2	16.4	8.2	0.39	0.6892
Error	10	213	21.3	—	—
Ethanol selectivity					
Repetition	2	0.10	0.05	0.86	0.4527
Protein (Pr)	1	0.24	0.24	4.01	0.0732
Temperature (T)	2	0.90	0.45	7.39	0.0107
Pr*T	2	0.74	0.37	6.08	0.0187
Error	10	0.61	0.06	—	—

CONCLUSION

Because no fouling of the polydimethyl-siloxane pervaporation membrane occurred, no changes in total flux and ethanol selectivity were caused by dissolved protein at a concentration of 10 g/L in a 2% w/w ethanol–water solution. Since these concentrations correspond to the composition of culture supernatant obtained from the yeast fermentation of the hydrolyzed forage, no fundamental incompatibility between these two processes needs to be apprehended. It may be reasonably asserted that when dissolved protein is involved in a system such as pervaporation, the effect of temperature on performance is more likely to be significant than the effect of pressure. Separation of ethanol from the supernatant of yeast-fermented hydrolyzed forage by pervaporation, directly without prior protein removal by ultrafiltration, appears to be feasible.

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