PERVAPORATION WITH COMPOSITE PVA MEMBRANES FOR THE DEHYDRATION OF BIOETHANOL: EFFECT OF VOLATILE ORGANIC IMPURITIES ON PERMEATION PROPERTIES

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Introduction

Reducing dependency on fossil fuels is a major economical and environmental challenge that stimulated the development of renewable energy sources such as bioethanol. At present, bioethanol fuel is used in several countries, in the form of its derivative ETBE (Ethyl Tertiary Butyl Ether) or blended with gasoline at a rate of 5% to 100% v/v.

Bioethanol needs to be dehydrated prior to its use as a fuel. According to EU directive 15376, the residual amount of water in bioethanol must not exceed 0.3% w/w. At present, the traditional techniques used for ethanol dehydration in the world industry include azeotropic distillation and dehydration on molecular sieves.

Pervaporation is a membrane process, largely described as a promising alternative to the traditional techniques of ethanol dehydration (1, 2). Indeed, pervaporation is considered as more flexible, cleaner and requiring less energy than these techniques. Numerous works have been carried out in order to study the performance of hydrophilic pervaporation (1, 3, 4). Most of them described studies performed using rectified ethanol (from fermented sugar cane or beet and starch) that has undergone several distillations to remove impurities. Ethanol obtained from agricultural residues and lignocellulosic biomass contains high amount of impurities, mainly volatile organic compounds (VOCs). The removal of VOCs by dedicated rectification increases the size and the energy consumption of the whole process. For example, the fermentation of grape marc produces bioethanol that contains up to 30000 ppm of methanol and some aldehydes and esters in smaller quantities. These VOCs can alter the performance of membrane processes used for ethanol dehydration.

This work was aimed to study the performance of commercial composite PVA membranes in dehydrating bioethanol, with a special focus on the effect of methanol, selected as a first model VOC, on permeation properties.

Materials and Methods

Pervaporation experiments

Pervaporation experiments were conducted using a laboratory-scale unit. The feed was placed in the heated vessel and recirculated using a volumetric pump. The recirculation flowrate was set at 100 kg.h^{-1}. The temperature was set at 60°C. The vacuum was applied on the shell side at 3 mbar. The unit was equipped with several digital sensors to monitor pressure, temperature, and flowrate.

PERVAP 1211 PVA (Polyvinyl alcohol) composite membranes were used (2-5 µm of active layer thickness, surface area of 170 cm²). Three different flat membranes (M1, M2 and M3) were tested. The permeate side was connected to a vacuum line and the permeate stream was condensed into two parallel cold traps maintained at -80°C. Permeate samples were then collected and weighted out. For each experiment, 10 kg of azeotropic bioethanol was used. Methanol (2% w/w) was added for some experiments. Fluxes and selectivity were calculated as following:

$$J = \frac{m}{At} \qquad J_i = \frac{D_i S_i}{z}(p_{i,f} - p_{i,p}) = Kapp(p_{i,f} - p_{i,p}) \qquad \alpha_{i,j} = \frac{yi/xi}{yj/xj}$$

where J is the total permeate flux, m the mass of the permeate, A the membrane surface area and t the permeation time. yi and yj are respectively the weight fractions of component i and j in the permeate. xi and xj are respectively the weight fractions of component i and j in the feed.

Partial fluxes were calculated using the total flux and the weight fraction of each component in the permeate. For a known partial flux, the apparent transfer coefficient K_{app} was obtained after determining the driving force ($\Delta p_i = p_{i,f} - p_{i,p}$) where $p_{i,f}$ is the partial pressure of component i in the feed (calculated using the Raoult's law) and $p_{i,p}$ is the partial pressure of component i in the permeate (calculated using the Dalton's law). Di and Si are the diffusivity and the sorption coefficient of the component i into the membrane. z is the membrane thickness under pervaporation conditions.

Analysis

Water concentration in feed and retentate samples was determined using Karl Fischer titration (756 KF Coulometer). Ethanol concentration in permeate samples was determined by HPLC analysis on a

P680 HPLC Pump DIONEX equipment using an ion exchange column (300 mm x 7.8 mm) with H_2SO_4 0.01 N as the mobile phase and propionic acid as the internal standard. The apparatus is coupled to a refractometer detector (410 Diff. Refract, Waters).

Methanol concentration was measured by gas chromatography through a direct injection in a CPG Agilent 6890 equipped with a split injector at 200°C, an auto sampler (Combipal, Varian), a flame ionization detector (220°C; H_2: 40 mL/min; air: 450 mL/min; makeup gas He: 33 mL/min) and a CP Wax 57-CB column (50 m x 0,25 mm x 0,2 µm; Agilent).

Results and Discussion

Table 1. Pervaporation of ethanol-water mixture (94% w/w of ethanol in the feed) at 60°C and 3 mbar.

Membrane	Kapp$_{ethanol}$ (*10^{11}) (kg.m^{-2}.s^{-1}.Pa^{-1})	$\Delta p_{ethanol}$ (Pa)	J$_{ethanol}$ (kg.m^{-2}.h^{-1})	Kapp$_{water}$ (*10^{11}) (kg.m^{-2}.s^{-1}.Pa^{-1})	Δp_{water} (Pa)	J$_{water}$ (kg.m^{-2}.h^{-1})	$\alpha_{water, ethanol}$
M1	6.68	40000	0.0096	175.79	6505	0.041	66
M2	6.53	40630	0.0096	198.18	5890	0.042	74
M3	3.46	40631	0.0053	83.00	5906	0.018	56

The calculation of driving force and transfer coefficient makes it possible to evaluate the contribution of each of them on the partial flows. Table 1 shows that the partial flow for ethanol is mainly determined by the driving force. This high magnitude of driving force comes from the high partial pressure of ethanol if the feed mixture. Water permeation occurs with a significantly higher flux with regard to ethanol thanks to its high transfer coefficient.

Comparison with literature results is not always straightforward due to differences in experimental conditions and in membrane properties such as crosslink density and nature. Nevertheless, even with some differences between the three membranes tested in this work (Table 1), it can be noticed that the membrane selectivity is near of that reported for PVA membranes (3, 4).

Table 2. Pervaporation of ethanol-water-methanol mixture (94% w/w of ethanol and 2% w/w methanol in the feed) at 60°C and 3 mbar.

Membrane	Kapp$_{ethanol}$ (x10^{11}) (kg.m^{-2}.s^{-1}.Pa^{-1})	$\Delta p_{ethanol}$ (Pa)	J$_{ethanol}$ (kg.m^{-2}.h^{-1})	Kapp$_{water}$ (x10^{11}) (kg.m^{-2}.s^{-1}.Pa^{-1})	Δp_{water} (Pa)	J$_{water}$ (kg.m^{-2}.h^{-1})	Kapp$_{methanol}$ (x10^{11}) (kg.m^{-2}.s^{-1}.Pa^{-1})	$\Delta p_{methanol}$ (Pa)	J$_{methanol}$ (kg.m^{-2}.h^{-1})	$\alpha_{water, ethanol}$
M1	9.96	39997	0.0143	239.94	5751	0.050	4.02	2027	0.000293	57
M2	10.80	39795	0.0155	223.30	5925	0.048	4.57	2057	0.000338	49
M3	9.30	40008	0.0134	103.89	5995	0.022	5.17	1568	0.000292	27

Table 2 shows that the permeation fluxes were increased after adding 2% w/w methanol to the feed. The increase in ethanol flux was more noticeable (60% for M2) than that observed for water (20%). The resulting selectivity for water was then decreased with regard to Table1. These results are directly related to the increase in transfer coefficient of both water and ethanol when methanol is added.

Methanol molecules did not seem to induce any competition effect with regard to water and ethanol molecules. Because of its low diffusive cross-section and hydrophobicity (data not shown), methanol would be considered to have better sorption and diffusion than ethanol, as reported in literature for binary alcohol-water mixtures (5). In this work, the transfer coefficient for methanol was lower than that obtained for ethanol and water. The resulting selectivity for methanol with regard to ethanol was near 1 (data not shown). Moreover, the low values of methanol flux exclude the hypothesis of coupling effect with water and ethanol permeation. It is then suggested that methanol molecules would be plasticized inside the membrane, inducing modification of membrane structure and swelling degree in a way that increases the permeability (D_ixS_i) to water and ethanol.

Conclusions

This work highlights the effects of methanol, considered as a first example of VOCs, on water and ethanol transfer in PVA hydrophilic membranes. These results have not yet been reported previously. Possible mechanisms involve modifications of the membrane structure and permeability. Further work is needed to better understand these mechanisms, by using other VOCs with selected properties and by modeling the membrane molecular dynamics.

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