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Procedia Engineering 44 (2012) 1173 – 1176

**Procedia
Engineering**www.elsevier.com/locate/procedia**Euromembrane Conference 2012****[P2.007]****Pervaporative dehydration of bioethanol using silica and PVA membranes: Analysis of permeation performances and effect of volatile organic impurities**M. Moussa, V. Athès*, Y. Imbert, I. Souchon, O. Vitrac, M.L. Lameloise et al
*INRA, France***Introduction**

Hydrophilic membrane pervaporation is largely described as a promising alternative to molecular sieves and azeotropic distillation, the ordinary techniques for ethanol dehydration (6, 7). Pervaporation is considered as more flexible, cleaner and less energy consuming technology.

Solvent dehydration, including ethanol, using pervaporation has been studied by several authors (2, 3, 6, 10, 11). Three major types of membranes have been studied: i) organic (polymeric) membranes, ii) inorganic (ceramic) membranes and iii) hybrid membranes that cover polymeric as well as inorganic membranes.

During the last 10 years, considerable efforts have been put in the development of inorganic and hybrid membranes as they show a better chemical, hydrothermal and mechanical stability and are free of swelling (10). Extensive research works have been focused on optimization of membrane material and operation parameters to maximize permeation flux and water selectivity (4, 8). However, most of these works reported permeation data without systematically analyzing the contribution of the intrinsic parameters, *i.e.* membrane permeability (adsorption-diffusion through the membrane) and driving force.

Polymeric membranes remain the most widely used for pervaporation in the industry. These membranes are attractive because of their economical and fabrication advantages. Polymers such as cross-linked poly-vinyl alcohol (PVA), polyimide and poly-acrylic acid are some of the materials used for the dehydration of ethanol and other solvents (2). Perm-selectivity performances of polymeric membranes are widely reported in the literature (5). Most of studies were performed using binary water-ethanol mixture that has undergone several distillations to remove volatile organic compounds (VOCs) impurities. Ethanol obtained from agricultural residues and lignocellulosic biomass contains high amount of impurities, mainly VOCs. 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, which can modify the perm-selectivity of polymeric membranes. Little is known about the performance of polymeric membranes in contact with complex mixtures, *i.e.* containing VOCs.

This work was aimed to study the performance of a silica and PVA commercial membranes used for the dehydration of bioethanol, with a closer look on mass transfer coefficients variation as a function of feed temperature, permeate pressure and water content in the feed. In the case of the PVA membrane, a special focus was made on the effect of methanol, selected as a first model VOC.

Materials and Methods

Pervaporation experiments were conducted using a laboratory-scale unit. The feed was placed in the heated vessel and recirculated using a volumetric pump. The feed flowrate was set at 100 kg.h⁻¹. The unit was equipped with several digital sensors to monitor pressure, temperature, and flowrate.

PERVAP 1211 (PVA, Sulzer Chemtech; flat surface area of 170 cm²) and Me-Si (Methylated silicium, Pervatech; surface area of 50 cm²) were the two membranes used. The permeate stream was condensed under vacuum into two parallel cold traps set at -80°C. Permeate samples were then collected and weighted out. For each experiment, 10 kg of azeotropic bioethanol (94%w/w) was used. Methanol (2% w/w) was added for some experiments with PVA membrane. Fluxes and selectivity were calculated as following:

$$J = \frac{m}{At} \quad J_i = \frac{D_i \cdot S_i}{z} (p_{i,f} - p_{i,p}) = K_{app} (p_{i,f} - p_{i,p}) \quad \alpha_{i,j} = \frac{W_{i,p}/W_{i,f}}{W_{j,p}/W_{j,f}}$$

where J is the total permeate flux, m the mass of the permeate, A the membrane surface area and t the permeation time. $W_{i,p}$ and $W_{j,p}$ are respectively the weight fractions of component i and j in the permeate. $W_{i,f}$ and $W_{j,f}$ 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 extensive Raoult's law) and $p_{i,p}$ is the partial pressure of component i in the permeate (calculated using the Dalton's law). D_i and S_i are the diffusivity and the sorption coefficient of the component i into the membrane. z is the membrane thickness under pervaporation conditions.

Water concentration in feed and retentate samples was determined using Karl Fischer titration. Ethanol concentration in permeate samples was determined by HPLC analysis. Methanol concentration was measured by gas chromatography.

Results and Discussion

Table 1. Pervaporation of ethanol-water mixture (94% w/w of ethanol) using methylated silicium membrane. Permeate pressure was set at 300 Pa.

Temperature	Ethanol			Water			$U_{water, ethanol}$
	$J_{ethanol}$ (*10 ⁵) (kg.m ⁻² .s ⁻¹)	$K_{app, ethanol}$ (*10 ¹⁰) (kg.m ⁻² .s ⁻¹ .Pa ⁻¹)	$\Delta p_{ethanol}$ (Pa)	J_{water} (*10 ⁵) (kg.m ⁻² .s ⁻¹)	$K_{app, water}$ (*10 ¹⁰) (kg.m ⁻² .s ⁻¹ .Pa ⁻¹)	Δp_{water} (Pa)	
30°C	0.54 ± 0.03	6.00 ± 0.43	9077 ± 007	3.56 ± 0.56	300 ± 39	1184 ± 008	111±5
60°C	1.65 ± 0.11	4.10 ± 0.27	40302 ± 229	17.33 ± 0.56	301 ± 07	5768 ± 191	169±9

The calculation of driving force (Δp_i) and transfer coefficient makes it possible to evaluate their contribution in the partial flux. Table 1 shows that, for ethanol, the partial flux ($J_{ethanol}$) is mainly determined by the high magnitude of driving force which comes from its high partial pressure in the feed mixture. For water, the high transfer coefficient produces a significantly higher flux in comparison with ethanol. The increase in temperature induces high increase in driving forces, mainly because of the increase in water and ethanol partial pressures in the feed, without significantly modifying the transfer coefficients. These results indicate that the adsorption and diffusion phenomena are not significantly modified as a function of temperature for the Me-Si membrane.

Table 2. Pervaporation of ethanol-water mixture (94% w/w of ethanol) using PVA membrane, with or without 2% w/w methanol in the feed. The feed temperature and permeate pressure were set at 60°C and 300 Pa respectively.

Feed mixture	Ethanol			Water			$Q_{\text{water, ethanol}}$
	$J_{\text{ethanol}} (^*10^5)$ ($\text{kg.m}^{-2}.\text{s}^{-1}$)	$K_{\text{app,ethanol}} (^*10^{10})$ ($\text{kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$)	$\Delta p_{\text{ethanol}}$ (Pa)	$J_{\text{water}} (^*10^5)$ ($\text{kg.m}^{-2}.\text{s}^{-1}$)	$K_{\text{app,water}} (^*10^{10})$ ($\text{kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$)	Δp_{water} (Pa)	
ethanol + water	0.27 ± 0.01	0.66 ± 0.02	40315 ± 617	1.17 ± 0.06	18.70 ± 2	6198 ± 603	68 ± 5
ethanol + water + methanol	0.41 ± 0.02	1.04 ± 0.08	39896 ± 198	1.36 ± 0.02	23.16 ± 1.6	5838 ± 121	53 ± 4

From comparison between tables 1 and 2 for the same operation and feed temperature at 60°C, it appears that the Me-Si membrane showed better perm-selectivity performances than those obtained for PVA membrane. Indeed, the ethanol and water driving forces for this latter membrane were weighted by lower transfer coefficients with regard to the Me-Si membrane.

Table 2 shows that water and ethanol permeation fluxes were increased after adding 2% w/w methanol to the feed. The increase in ethanol flux was more noticeable than that observed for water. The resulting selectivity for water was then decreased with regard to the binary mixture. These results are directly related to the increase in transfer coefficient of both water and ethanol when methanol is added. Moreover, 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 (3, 9), methanol would be considered to have better sorption and diffusion than ethanol, as reported in literature for binary alcohol-water mixtures (3). In this work, the transfer coefficient for methanol was lower than that obtained for ethanol and water and the resulting selectivity for methanol with regard to ethanol was near 1 (data not shown). 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 ($D_i \times S_i$) to water and ethanol. This hypothesis is supported by data from literature about the higher density of H-bonds between PVA and methanol in comparison with water and ethanol molecules (1). Further work is needed to better understand these phenomena, by using other VOCs with selected thermodynamic properties and by modeling the membrane molecular dynamics.

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Keywords: pervaporation, bioethanol, dehydration, membrane