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# IMPLEMENTATION OF PERVAPORATION IN BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC MATERIALS

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**Abstract**

*Production of ethanol from lignocellulosic biomass has a high potential concerning substrate availability compared to substrates containing starch for the development of non-fossil fuel energy sources. In this case, low concentration bioethanol is gained by yeast fermentation and it has to be efficiently recovered and concentrated. Cost effective separation technologies are needed to reduce the energy demand for the whole production process. The membrane separation process pervaporation is a very promising option to achieve this goal.*

**Key words***: pervaporation, bioethanol, recovery, lignocellulosic biomass*

## 1. INTRODUCTION

Pervaporation is a membrane process for liquid separation where a polymeric or zeolite membrane usually serves as barrier for the separation (Feng and Huang, 1997). To date, pervaporation has found viable applications in dehydration of organic solvents, removal of dilute organics from aqueous streams and separation of organic-organic mixtures. Because of the increasing pressure to use biofuels (such as ethanol) to improve petroleum-combustion efficiency, significant amounts of renewable carbon sources as starting material for the production of bioethanol are required. Lately, the utilization of lignocellulosic materials to obtain ethanol has gained much attention. Lignocellulosic biomass includes side product or biomass waste from other processes, e.g. pulp and paper sludge (Sosulski, 1994), fruit and vegetables processing wastes (Korkie et al., 2002), wood chips and thinnings (Kadam et al., 2000). In this biomass-to-ethanol process lignocellulosic biomass is converted into sugars which are then fermented to ethanol. The obtained fermentation broth contains about 2 % w/w ethanol (Belkacemi et al., 1998). In this case, the conventionally applied distillation is not practical with ethanol solutions of such low concentration and pervaporation is considered as an alternative to recover ethanol from these fermentation broths. According to the literature, rubbery-based membranes have found wide use in this application, because of their high affinity and low transport resistance for organics (Shao and Huang, 2007).

In this paper, the influence of different parameters on the ethanol recovery from dilute alcohol-aqueous solutions by means of pervaporation is reported, using a hydrophobic flat-plate poly(octhylmethyl siloxane) membrane [POMS].

## 2. MATERIALS AND METHODS

99.5% ethanol (Merck Co. Ltd.) and de-ionized water were used to prepare ethanol-aqueous solutions. POMS-PAN membrane employed in this study was made of poly(octhylmethyl siloxane) silicone

rubber skin layer on poly(acrylonitrile) support and was kindly supplied by GKSS (Geesthacht, Germany).

Pervaporation experiments were performed on lab-scale pervaporation equipment schematically shown in Fig. 1. The ethanol-aqueous solution (feed) was pumped from a reservoir (2) towards the membrane by a gear pump (3) and recirculated at a flow rate of 97 L $h^{-1}$. The flat-plate membrane with effective surface area of 0.0288 $m^2$ was placed in a stainless steel module (5). Feed temperature was maintained by a thermostated water bath (1) and controlled by a temperature sensor (T). Feed was kept at atmospheric pressure, whereas the desired permeate pressure was maintained by an oil sealed vacuum pump (8). Permeate vapour was condensed and collected in a Pyrex glass kept in cold trap (6) filled with liquid nitrogen.

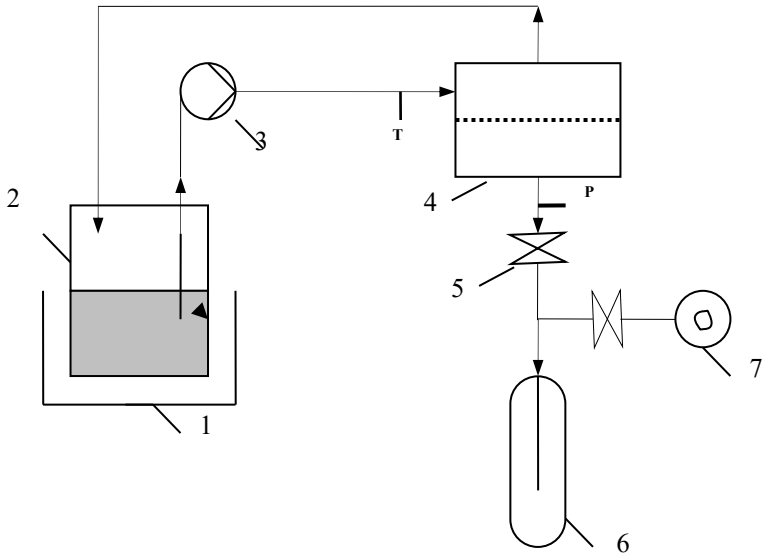


**Fig. 1**. Schematic diagram of the pervaporation set-up: 1 – thermostated water bath; 2 – feed tank; 3 – feed recirculation pump; 4 – pervaporation module; 5 – valve; 6 – cold trap; 7 - vacuum pump; T – temperature sensor; P - pressure sensor.

Ethanol concentration was determined by measuring relative density on a density meter (Mettler Toledo, Switzerland). Flux (J) and selectivity, expressed by separation factor (α), were calculated as follows:

$$J = \frac{M}{A\,t} \tag{1}$$

$$\alpha = \frac{y_{EtOH} / y_{H_2O}}{x_{EtOH} / x_{H_2O}} \tag{2}$$

where J (kg $m^{-2}$ $h^{-1}$) is permeate flux, M is permeate weight (kg), A is effective membrane area ($m^2$), t is pervaporation time (h); α is ethanol to water separation factor (dimensionless), y and x are weight fractions of the components in feed and permeate, respectively.

## 3. RESULTS AND DISCUSSION

The effects of feed composition, feed temperature and permeate pressure on the pervaporation performance were studied using dilute ethanol-water mixtures. All experiments were conducted in batch mode for 1.15 h; feed flow rate was kept constant at 97 L $h^{-1}$.

Results are shown in terms of permeate flux and ethanol to water separation factor.

### *3.1. Effect of feed composition*

Pervaporation transport is described by the solution-diffusion model and according to it both sorption and diffusion of the components in the membrane characterize the membrane properties (Khayet, 2008). A change in feed composition directly affects the sorption at the liquid-membrane interface. The diffusion of the components in the membrane is dependent on their concentration, so permeation characteristics are also dependent on feed composition (Huang, 1991). Therefore, the effect of feed solution composition was investigated by varying ethanol concentration in the range from 0.5 % w/w to 10 % w/w. The data obtained are shown in Fig. 2 and 3.

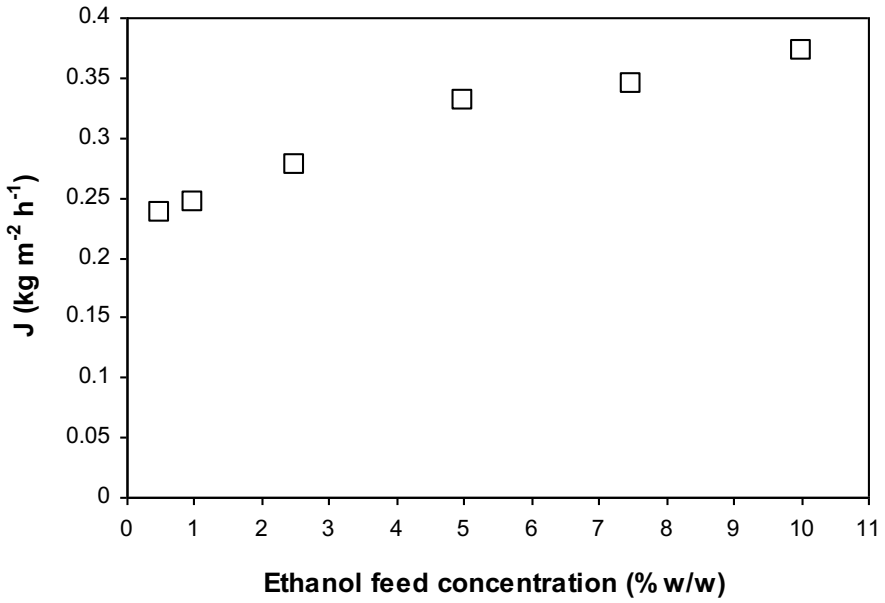


**Fig. 2.** Effect of ethanol feed concentration on permeate flux
( feed temperature 75 °C; vacuum pressure 25 mbar; feed flow rate 97 L $h^{-1}$)

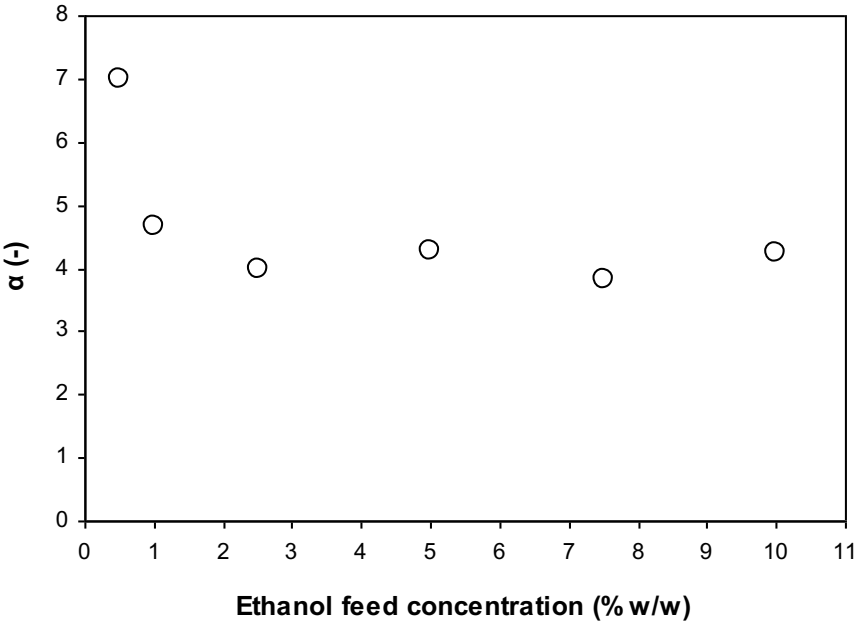


**Fig. 3.** Effect of ethanol feed concentration on ethanol-water separation factor (feed temperature 75 °C; vacuum pressure 25 mbar; feed flow rate 97 L $h^{-1}$)

It can be seen that the flux gradually but constantly increases with increasing alcohol concentration (Fig.2). This can be explained with better ethanol sorption properties of the membrane at higher alcohol concentrations. The membrane becomes more swollen and flux slightly increases. Consequently, when increasing alcohol concentration, there is a reduction in separation factor (Fig.3) which is most significant at ethanol concentrations between 0.5 % w/w and 2.5 % w/w.

*3.2. Effect of feed temperature*

Since solubility and diffusivity of the feed components in polymeric membranes are generally dependent on the operating temperature, the flux is also dependent on it. Thus, pervaporation experiments at different feed temperatures between 25 and 95 °C were carried out.

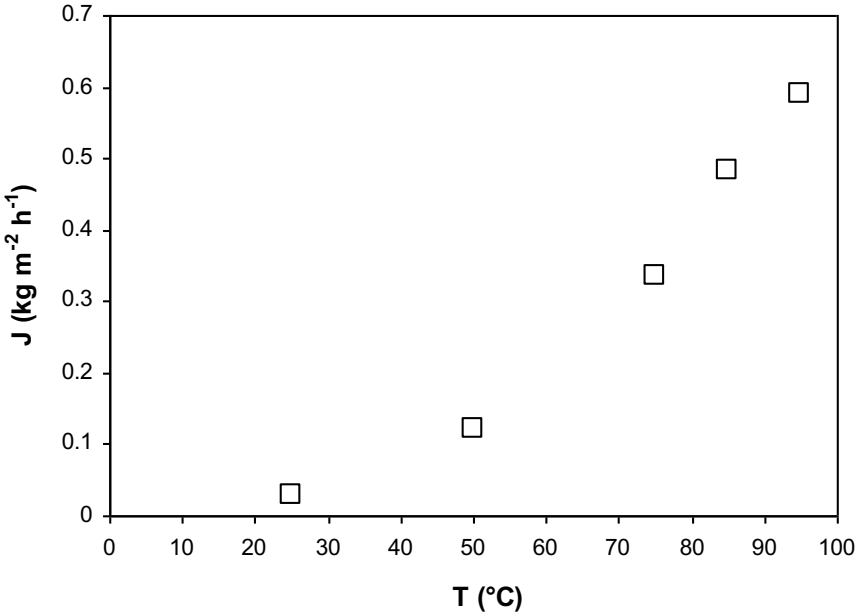


**Fig. 4.** Effect of feed temperature on permeate flux
(vacuum pressure 25 mbar; feed flow rate 97 L $h^{-1}$; ethanol feed concentration 5 % w/w)

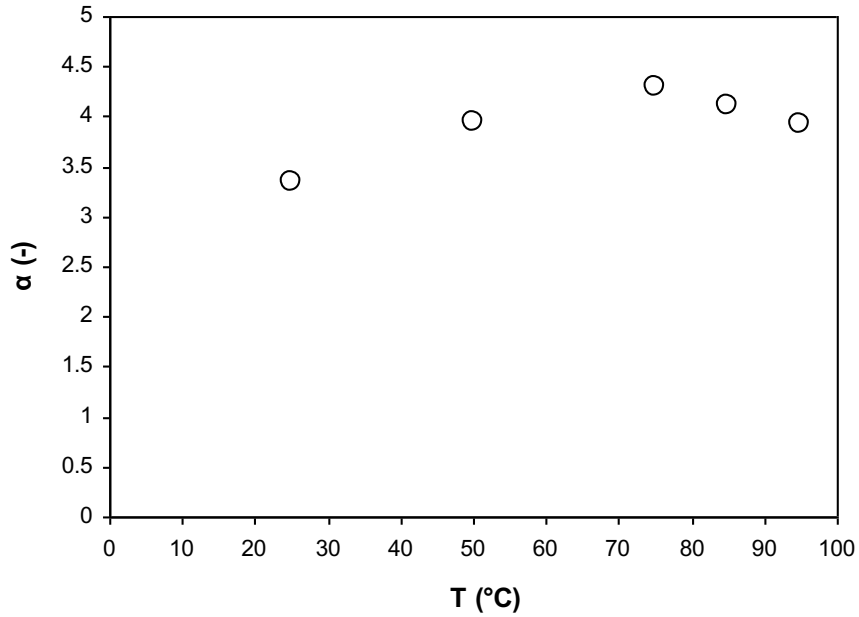


**Fig. 5.** Effect of feed temperature on ethanol-water separation factor
(vacuum pressure 25 mbar; feed flow rate 97 L $h^{-1}$; ethanol feed concentration 5 % w/w)

In Fig. 4 and 5 permeate flux and separation factor, respectively, are plotted against operating temperature. As can be seen, the flux is strongly affected by the temperature and continually increases in the whole temperature range studied (Fig.4). At higher temperatures the mobility of the polymer

chains increases, producing larger membrane-free volumes (i.e. membrane swelling) and diffusion of the permeating molecules is enhanced.

*3.3. Effect of permeate pressure*

Permeate pressure is directly related to the activity of the components at the downstream side of the membrane, therefore, strongly affecting the pervaporation characteristics (Huang, 1991). Pervaporation experiments at permeate pressures of 25, 50, 75, 100 and 125 mbar were conducted and the data obtained are illustrated in Fig. 6. There is negligible difference in total flux values when working at 25 mbar and 50 mbar. Further increase in downstream vapour pressure from 50 mbar to 125 mbar leads to constant decrease in transport driving force, resulting in reduction of the flux.

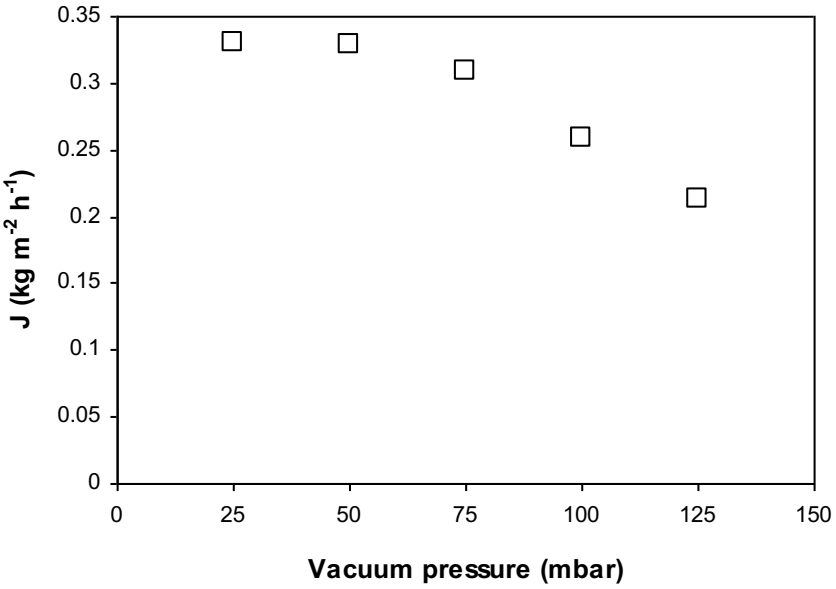


**Fig. 6.** Effect of vacuum pressure on permeate flux
(feed temperature 75 °C; feed flow rate 97 L $h^{-1}$; ethanol feed concentration 5 % w/w)

Fig. 5 reveals the effect of operating temperature on separation factor. Two temperature-ranges can be differentiated in which the separation factor is influenced by the temperature in different ways. In the first one (from 25 °C to 75 °C) the higher temperature results in higher separation factor values. In the second range, further increase in the temperature (from 75 °C to 95 °C) leads to reduction of the separation factor and at 95 °C its value is approximately as that at 50 °C (about 4.0). This trend could be explained as follows: when increasing the temperature up to 75 °C, both ethanol and water partial fluxes increase proportionally, while at higher temperatures water partial flux increases drastically and separation factor decreases.

Evidently, selectivity is also affected by the downstream pressure (Fig.7). There is a minimum value of the separation factor at vacuum pressures between 50 mbar and 75 mbar, then the separation factor values increase with further increase in permeate pressure. This is because of the existing trade-off between membrane permeability and selectivity. At higher vacuum pressure the increase in selectivity appears to be accompanied by lower permeability.

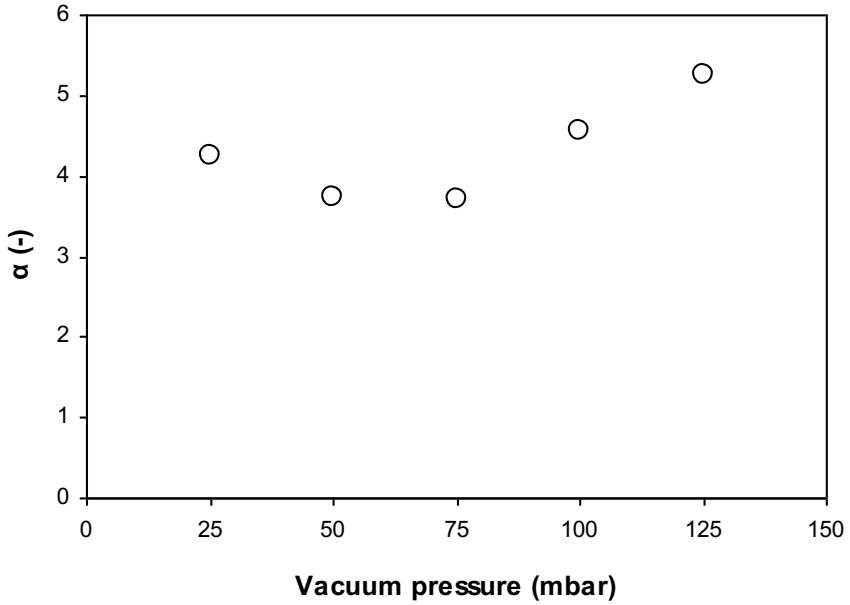


**Fig. 7.** Effect of vacuum pressure on ethanol-water separation factor
(feed temperature 75 °C; feed flow rate 97 L $h^{-1}$; ethanol feed concentration 5 % w/w)

## 4. CONCLUSIONS

Pervaporation experiments using poly(octhylmethyl siloxane) [POMS] membrane were carried out for separation of dilute ethanol-aqueous solutions. The results obtained demonstrated that the membrane was preferentially permeable to ethanol over water. Stable overall membrane performance was observed in the whole temperature range studied. The highest separation factor value of nearly 7.0 was attained at 0.5 % w/w ethanol concentration in feed solution. For the 5 % w/w ethanol mixture the highest membrane flux of 0.59 kg $m^{-2}$ $h^{-1}$ was achieved at feed temperature of 95 °C.

From the data received it could be concluded that POMS membrane is especially suitable for ethanol separation from dilute ethanol-aqueous solutions and could be used for the recovery of ethanol from fermentation broths of lignocellosic biomass in the process of production of ethanol as biofuel.

## ACKNOWLEDGEMENTS

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