ORIGINAL PAPER

Determination of optimum operational conditions for pervaporation of binary mixture water/1-propanol and ternary mixture water/1-propanol/propionic acid

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Abstract

This paper presents the performance of a commercial pervaporation membrane Pervap 2210 D, from Sulzer Chemtech GmbH (Germany) that was experimentally tested for the dehydration of binary mixtures:water/1-propanol; water/propionic acid and ternary mixtures: water/1-propanol/propionic acid. Pervap 2201D is a hydrophilic polymeric membrane consisting of a polyvinylalcohol (PAN) active layer and a support layer of polyacrilonitrile. The main characteristics of the membrane: permeability, selectivity and stability were evaluated using a pervaporation experimental scale unit. The influence of different experimental conditions on the membrane efficiency such as feed water concentrations (5-20 wt-%), feed temperatures (60-80º C), permeate pressure (15-40 mbar) and different propionic acid concentrations in the feed (10-95 wt-%) were investigated. The results of the experiments indicate that high values of permeate fluxes are obtained when increasing feed water concentration and temperature, and also at lower permeate pressure. The permeate water concentration was between 96-100 wt-% and these values indicate a good selectivity of the membrane for water. The permeability and selectivity of the polymeric membrane in acid conditions was not significant affected in the presence of 10-45 wt-% of propionic acid in the feed mixture. The results of permeate analysis of the binary mixture experiments with the composition of 5 wt-% water and 95 wt-% propionic acid indicate the presence of 25 wt-% propionic acid in the permeate concentration, accompanied by an increase of the total fluxes and an decrease of the membrane selectivity.

Introduction

Even if the most used separation technology in the chemical industry is distillation, the importance of alternative techniques is continuously increasing. Nowadays industry move to incorporate pollution prevention principles into their production processes and make efforts to remediate existing contaminated sites and waste streams. Thus improvements in the efficiency of the conventional separation processes and integration of new cost-effective separation technology are needed. Membrane technologies can be used to separate, fractionate, and concentrate contaminants or process components obtained from chemical or biotechnological processes [1].

Generally, membrane processes require minimal temperature changes and chemical additions, operate in either continuous or batch modes, use significantly less energy than traditional separation processes, do not alter the chemical structure of the processed materials, and are easy to integrate into existing processes due to their modular nature and compact size. During the last decade, pervaporation (PV) has established itself as one of the most promising membrane technologies. Pervaporation is a membrane process, where the components change their aggregate state from liquid to vapor while permeating. Thus, it is a costly process with a high-energy demand compared to other membrane techniques that are realised in liquid solutions. However, its energy demand is small when compared with distillation, and in many cases pervaporation or pervaporation combined with other separation processes is an economical alternative for separation of different mixtures of solvent production [2].

The literature about pervaporation processes is extensive and covers various aspects of pervaporations such as transport principles, process thermodynamics, the development of new membrane materials, industrial applications and improvement of the process designs to maximise the performance in terms of separation factor, flux and stability [3-7].

Frequently, pervaporation has been used for dehydration of alcohols or other solvents with hydrophylic membranes [8-11]. There are also some other applications such as organic/water or organic/organic mixture separations using hydrophobic pervaporation [12-19]. The opportunity to use hydrophobic pervaporation in wastewater treatment has been widely recognized. In this type of application pollution control and solvent recovery are realized simultaneously. Examples are the recovery of phenol or chloroform from wastewater removal of chlorinated hydrocarbons from aqueous solutions [20].

Applications in biotechnologies (food industry and fermentations processes) are fruit juice aroma recovery, bear dealcoholisation in the food industry, product recovery from fermentation broths and enhanced bioconversions. 1-propanol, propionic acid and other organics can be obtained by chemical reactions or by fermentation with different microorganisms. The actual limited amount of chemicals obtaining through fermentation processes is mainly due to low process productivity and difficulties in product separation. Thus new processes as membrane separation can improve the productivity of different organics by fermentation processes [21-22].

Another application of pervaporation is related to the pollution caused by transport. Engine emissions, particularly from cars and trucks have been linked with severe damages to the environment and human health. The reserves of nonrenewable resources are considered almost depleted, because 80% of the fossil fuels supply has been used [23]. Instead of these resources, alcohols by fermentation from biomass represent one of the alternatives of the clean energy generation. In some countries, automobiles are already using ethanol instead of gasoline [24].

In order to be used efficiently a membrane should have a good selectivity accompanied by an acceptable flux of water for the dehydration of any mixtures by PV. The choice of the membrane material strongly depends on the type of application. It is important which component should be separated from the mixture and whether this component is water or another organic liquid. Generally, the component with the smallest weight fraction in the mixture should be preferentially transported across the membrane. Non-porous polymeric membranes, membrane made of conducting polymers as well as ceramic membranes are used in pervaporation [25].

One of the most used membranes for the dehydration of alcohols is a cross-linked polyvinyl alcohol (PVA) membrane. Such a membrane has been used for producing absolute alcohols on an industrial scale [26].

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The pervaporation performance of the membrane can be evaluated in terms of permeation flux and selectivity. According to the experimental results, the permeate fluxes (total and partial fluxes) have been calculated by using the following formulas [5, 26]:

$$J_{tot} = \frac{m_{permeate}}{\Delta t_{exp} \cdot A_{membrane}}$$

(1)

The partial flux of one component through a membrane is introduced as a total flux times the mass fraction of the component in permeate:

$$J_i = J_{tot} \cdot w_i^P$$

(2)

Where:

J_{tot} is the total permeate flux (Kg/m$^2\cdot$ h);

$A_{membrane}$ is the effective area of the membrane (m^2);

Δt_{exp} is the time of one experiment (h), J_i is the partial permeate flux of component i

(Kg/m$^2\cdot$ h); w_i^P are the weight fraction of component i in the permeate.

The selectivity of the pervaporation process is defined as the ratio of permeate composition to feed compositions (separation factor):

$$\alpha_{mix} = \frac{w^P_A / w^F_A}{w^P_B / w^F_B}$$

(3)

Since there is usually a trade-off between membrane permeability and selectivity, Huang and Rhim, 1991 [27], introduced a composite parameter to evaluate the performance of a membrane to separate a certain component, namely the pervaporation separation index (PSI), which is expressed as:

$$PSI = J_i(\beta - 1)$$

(4)

$$\beta = \frac{w^P_A}{w^F_A},$$

(5)

Where: w_A^P and w_B^P are the weight fractions of component A and B in the permeate;

w_A^F and w_B^F are the weight fractions of component A and B in the feed;

β is the separation factor of the faster permeating species (in this case the faster permeating species is water).

This study considers the evaluation of different experimental factors such as: feed concentration, temperature, permeate pressure and type of mixture: binary and ternary, so as to determine the efficiency of pervaporation process in term of permeability, selectivity and stability. Dehydration by pervaporation of binary and ternary mixture (1-propanol/water; propionic acid/water and water/propionic acid/ 1-propanol) was investigated using a plate module with a polymeric membrane Pervap 2201 D commercialized by Sulzer Chemtech GmbH, Germany. The feed mixture was chosen considering the synthesis of propyl propionate using the hybrid process: reactive distillation combined with pervaporation. A pervaporation module can be coupled on the top, middle or bottom of a distillation column

(function of the mixture to be separated) to increase the efficiency of the process and to decrease the energy consumtion.

Materials and methods

The membrane used in this study is a hydrophilic polymeric membrane consisting of a polyvinyl alcohol (PVA) active layer and a support of polyacrilonitrile (PAN). The membrane has an area of 0.0162 m^2 and can be used at temperatures up to $100°$ C, the maximum water content is 80%, has no limitation in the presence of organic acids and a limitation of 3% in the presence of inorganic acids.

All pervaporation experiments were carried out with a laboratory scale plant from Dortmund University, Chair of Fluid Separation Processes, [28, 29]. The chemicals used for experimental investigation were obtained from Merck Company, Germany, with the purity of 99.97%. The experimental equipment is presented in figure 1.
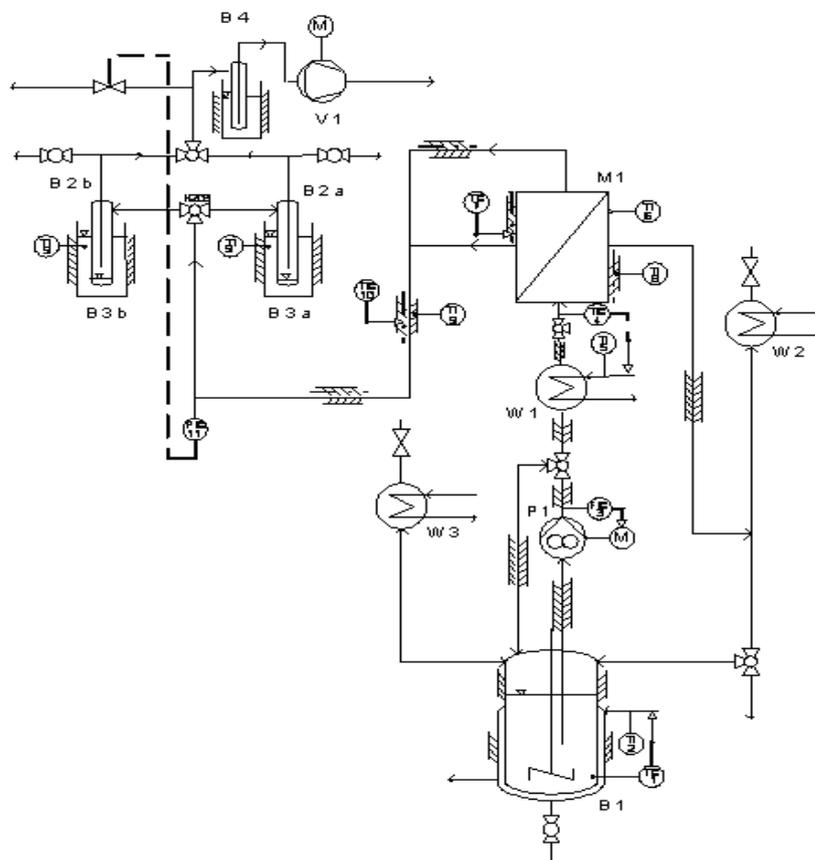

Figure 1. Pervaporation plant flow diagram

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B 1:	Reactor; M 1: Membrane	FIC 3:	Measurement Controller of the Flow
P 1:	Gear Pump; V 1: Vacuum Pump	TIC 4:	Temperature Controller of the Preheater
W 1:	Pre-heater;	TI 5:	Temperature Indicator of Oil for the Preheater
B 2, 3:	Cooling Traps Permeate	TI 6:	Heating Band Temperature Indicator
B 4:	Cooling Traps for Vacuum Pump	TIC 7:	Temperature Controller for the Heating Bands
TIC 1:	Temperature Controller of the Reactor	TI 8:	Module Temperature Indicator
TI 2:	Temperature Indicator of Oil for the Reactor	TI 9:	Permeate Heating Band Temperature Indicator
		TIC 10:	Temperature Controller of the Permeate Heating Band

The binary experiments water/1-propanol were performed at different feed concentrations within the interval of 5-20 wt-% water, in the case of experiments which describe the influence of water feed concentration and working temperature. In this case, the permeate pressure was kept constant at 20 mbar and the feed pressure was 1.013 bar. The flow rate of the feed pump was about 100 l/h. The range of feed temperature was chosen between 60-80° C.

Experiments at two different permeate pressures, 15mbar and 40 mbar at an initial feed water content of 12.5% and feed temperature of 75° C were performed to analyze the permeate pressure influence on the permeate fluxes.

Ternary mixture experiments with different concentrations of propionic acids in the feed (10-45%) were performed in order to analyze the influence of the third component over the total permeate fluxes.

Influences of acid conditions on membrane performance were observed with two procedures. First, after ternary experiments with maximum 45 wt-% propionic acid in the feed mixture, binary experiments with 1-propanol/water were repeated in the same operational conditions as in the ternary mixture experiments.

In the second procedure, the behavior of membrane in contact with mixtures containing very high concentration of propionic acid was investigated. Initially, by using a new membrane, binary experiments with 10 wt-% water and 90 wt-% 1-propanol were performed, followed by experiments with 5 wt-% water and 95 wt-% propionic acid. Afterwards, the experiments with 1-propanol/water were repeated with the same feed concentration and operational condition: 75° C, permeate pressure 33 mbar, feed pressure 1.013 bar, flow rate around 100 l/h.

Feed and permeate analysis

Feed concentration is given by the reactor mixture concentration. Water content in the feed samples were analyzed using a Karl Fisher Titrator (KF) from Metler Toledo, model DL 31 and a Shimatzu Gas Chromatograph (GC) with Flame Ionisation Detector. Because of the high content of water, the permeate sample were analyzed just by GC. For a good relevance of the results, each sample was twice analyzed and the final value was given by the average between the KF results and GC results. The feed water content used further in graphics was calculated as an average value between the sample taken at the initial and the final time of one experiment.

Results and discussion

Influence of water feed concentration and temperature.

In figure 2, the total permeates fluxes and the water concentrations are plotted as a function of the feed water concentration and the feed temperature. It can be observed that the permeate flux increases almost linearly with the water feed content. Also, a temperature increase leads to high values of permeate fluxes. At feed water concentrations of 5 wt-%, the permeate water concentration is around 96 wt -% but it increases even until100 wt -%, when the temperature and feed water concentration increase.

Figure 3 represents the variation of the separation factor (α_{mix}) of the pervaporation process function of temperature and the corresponding PSI. Figure 4 represents the variation of separation factor of the pervaporation process as a function of feed water concentration and the corresponding PSI. It can be observed that high values of temperatures (60-80° C) and feed water concentrations (5-20 wt-%) leads to high values of PSI but to smaller values of separation factors. The values of PSI and α_{mix} are calculated using equations 3 and 4 and the curves presented in the figure 3 and 4, are the polynomial regression of the calculated values.
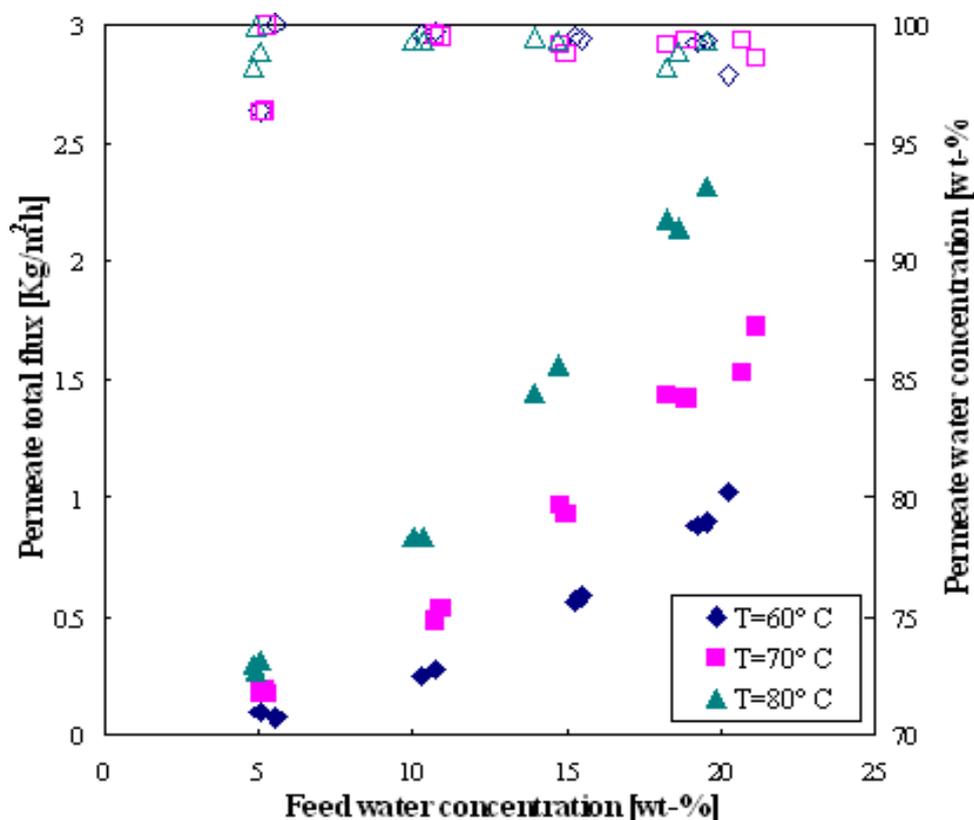
Figure 2. Permeate fluxes as a function of feed concentration at different temperatures for the system 1-propanol/water. The full symbols are measurements of the total permeate fluxes and open symbols are for the corresponding permeate water concentration.

Influence of permeate pressure

The influence of the permeate pressure on the separation characteristics of Pervap 2201 D membrane is illustrated in figure 5 for the system 1-propanol/water. The experiments

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were performed in the same operational conditions: water feed concentration range 7-13 %-wt, feed temperature of 75° C, flow rate of 100 l/h. It was observed that high permeate fluxes and permeate water concentrations are obtained at low permeate pressure.

In figure 6 is represented the variation of the separation factor (α_{mix}) of the pervaporation process and the PSI as a function of permeate pressure. It was observed that at low permeate pressure (15 mbar) the separation factor of the pervaporation process and the PSI values are higher than at 40 mbar. The decrease of the separation factor for mixtures 1-propanol/water with feed water concentration and temperature is also reported in previous studies [25, 26, 30, 31, 32].
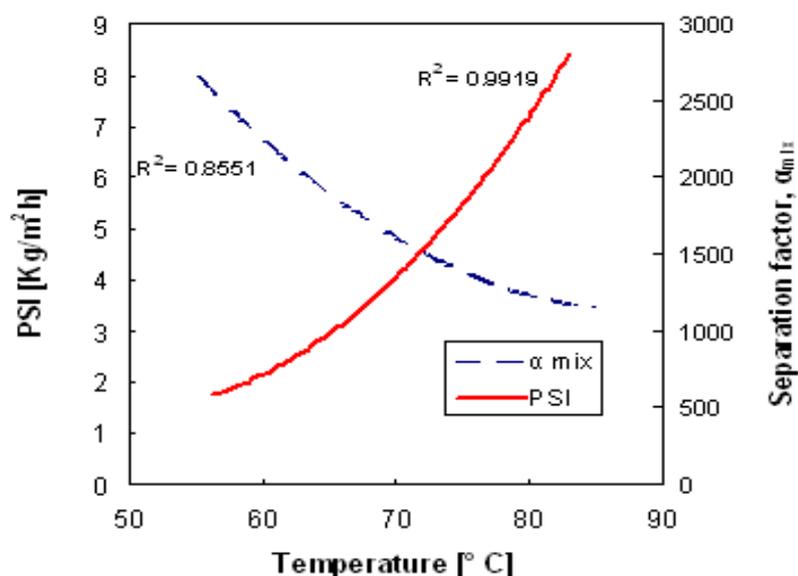

Figure 3. PSI and α_{mix} function of temperature (at feed water concentration of 10 wt-%)
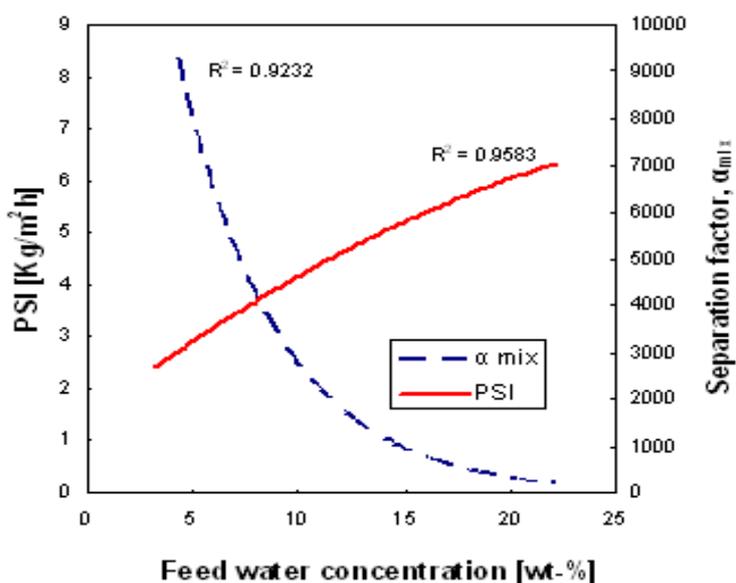

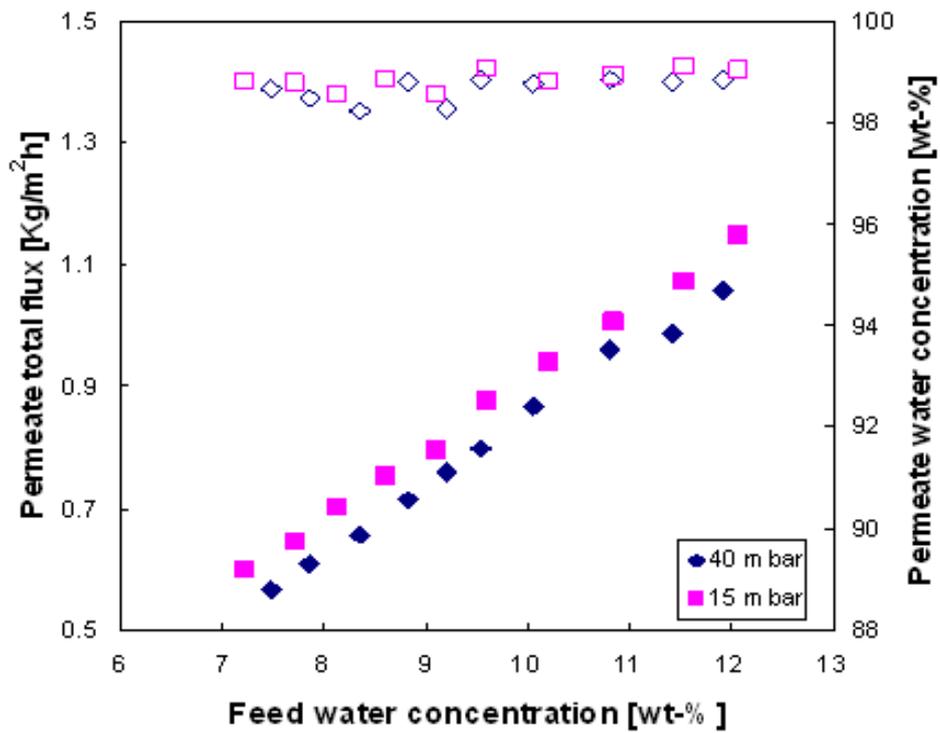**Figure 4.** PSI and α_{mix} function of feed water concentration at 70° C

Figure 5. Influence of permeate pressure on permeate fluxes. Filled symbols are measurements of total permeate fluxes and empty symbols represent the corresponding permeate water concentration
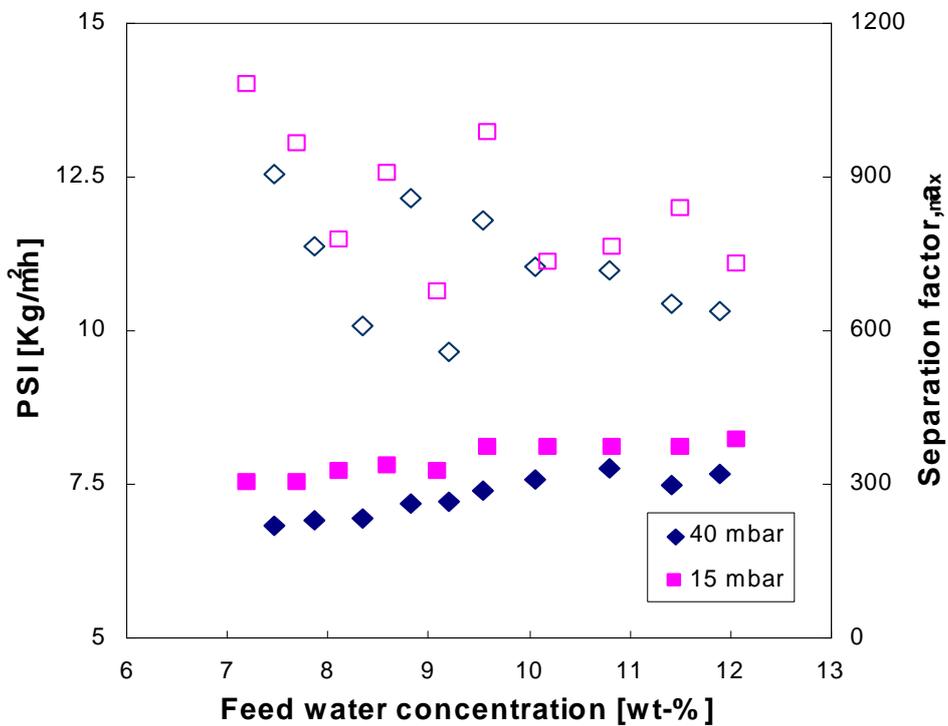

Figure 6. Pervaporation separation index function of feed water concentration at different permeate pressure. Filed symbols are the values of PSI and open symbols represent the corresponding separation factors

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Table 1 presents some experimental results from available literature about dehydration of water/1-propanol mixtures with different type of membrane materials and modules configuration, at different operational conditions and the results were interpreted in terms of permeate total fluxes and separation factor. The differences in fluxes and separation factors are mainly due to different permeate pressures and to different membrane materials used. As it can be observed, there are not so many studies for the determination of the separation characteristics of the binary mixture 1-propanol-water.

Table 1. Experimental results available in literature for binary mixture water/1-propanol

| Membrane type	water wt-%	T (°C)	P (mbar)	J_{tot} (kg/m^{2}h)	α	Reference
PVA cross linked with citric acid	10	30	1.3	0.078	141	[26]
polyvinylamine/polyvinylsulphate	10	58.6	0.2	1.2	6000	[30]
αAl$_2$O$_3$/PVA	10	70	10	2.2	50	[31]
PVA/PAN	5	60	-	0.15	90	[32]
Pervap 2201D (PVA/PAN)	10	60	20	0.26	2500	this study
	10	70	20	0.52	500	

Influence of propionic acid on the membrane selectivity

The experiments for dehydration of mixture water/1-propanol/propionic acid with various concentration of propionic acid between 10-45%-wt show that, in the presence of propionic acid, the permeate fluxes are not drastically changed (figure 7), but a decrease in the selectivity of the membrane was observed with the increase of propionic acid concentration.

Figure 8 presents a comparison of permeate fluxes of the ternary systems compared to fluxes of the corresponding binary system. Experiments with binary mixture 5 wt-% water and 95 wt-% propionic acid show high values of permeate fluxes compared to binary system 1-propanol/water or ternary mixture 1-propanol/water/propionic acid. Also, the permeate analysis indicate around 25 wt-% propionic acid in the permeate.

Figure 9 presents the permeate fluxes corresponding to experiments at different feed concentrations which were performed before and after experiments with propionic acid. The results of these experiments showed a significant change of permeate fluxes after experiments with 95 wt-% propionic acid. After experiments with ternary mixtures with 45 wt-% propionic acid, the increase of permeate fluxes was not significant. Also, the water concentration in permeate is decreasing with increasing feed concentration of propionic acid, from 99 wt-% permeate water concentration before experiments with propionic acid to 97.5 wt-% after experiment with 45 wt-% propionic acid in the feed.

In figure 10 is represented the evolution of the separation factor and PSI values as a function of experimental time. Experiments were run discontinuously, each experiment was stopped after 8-10 h operation time and the experimental plant was switched off over night. The selected values of separation factor and PSI were obtained from the experiments performed at 10 wt-% feed water concentration, at 75° C, permeate pressure 30 mbar, before and after experiments with propionic acid. The time given in this figure is the membrane operation time.
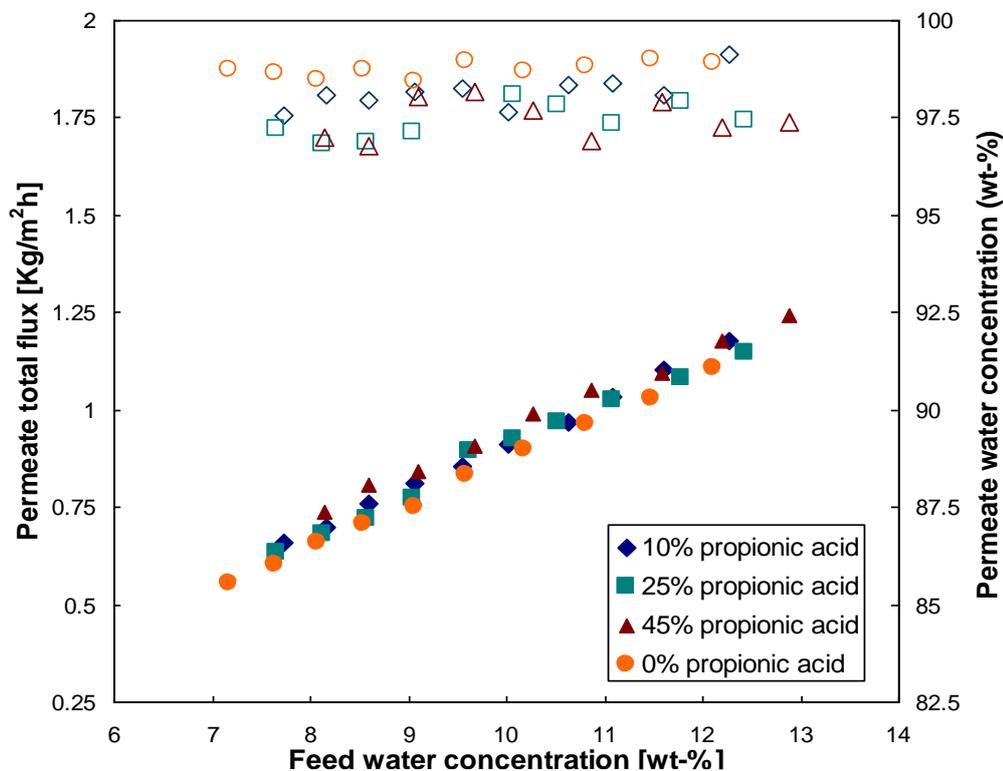
Figure 7. Permeate fluxes for ternary mixture: water/1-propanol/propionic acid at different propionic acid concentrations in feed compared with binary mixtures water/1-propanol. Filled symbols are permeate fluxes measurements and empty symbols are the corresponding permeate water concentration.

These experiments demonstrate that the selectivity of the polymeric membrane Pervap 2201 D is affected in the presence of high concentrations of propionic acid by increasing the permeate fluxes and decreasing the permeate water concentration. In industrial applications, such as the synthesis of propylpropionate from 1-propanol and propionic acid by the hybrid process: reactive distillation and pervaporation or vapourpermeation, it is not necessary to work at 95 wt-% propionic acid in the feed. The concentration of propionic acid in the feed mixture can be between 5-20 wt-% [33].

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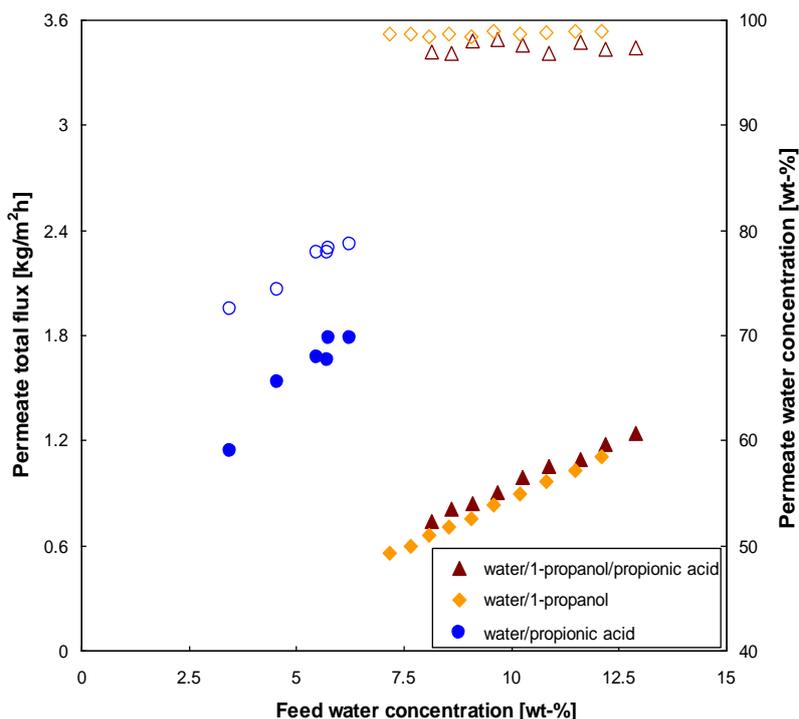
Figure 8. Permeate fluxes for ternary mixture: water/1-propanol/propionic acid at 45 %-wt propionic acid concentrations in feed compared with binary mixtures water/1-propanol and water/propionic acid. Filled symbols are permeate fluxes measurements and empty symbols are the corresponding permeate water concentration.
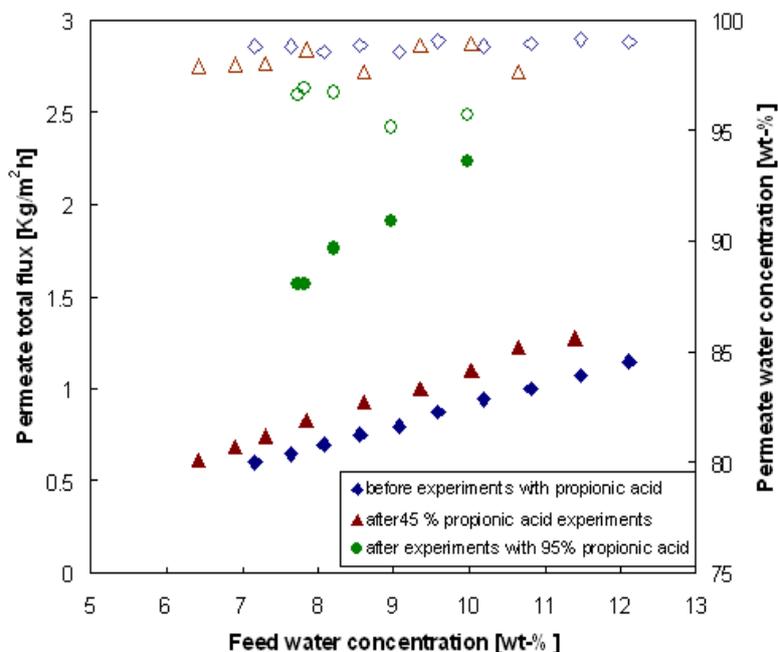
Figure 9. Permeate fluxes and permeate water concentration before and after experiments with propionic acid. Filled symbols are permeate fluxes measurements and empty symbols are the corresponding permeate water concentration.
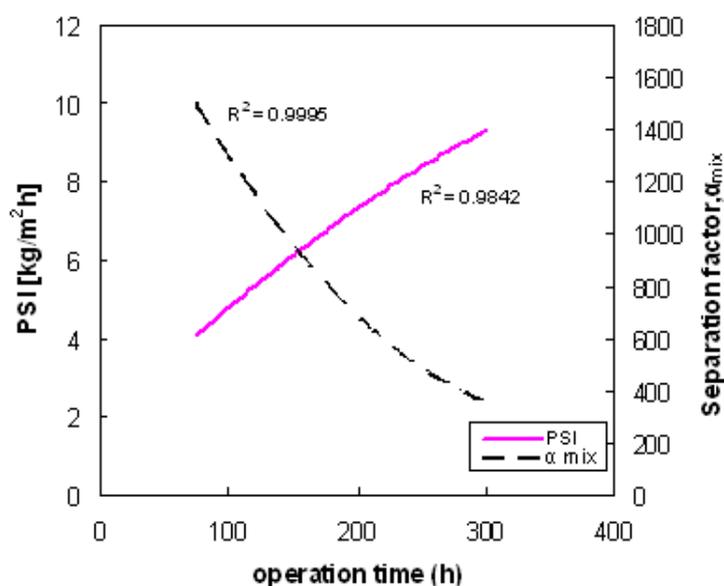
Figure 10. Separation factor of the pervaporation process and the PSI function of operation time

Conclusions

The performance of a polymeric commercial pervaporation membrane Pervap 2210 D, from Sulzer Chemtech GmbH (Germany) was experimentally tested for the dehydration of binary (water/ 1-propanol) and ternary mixtures (water/ 1-propanol/propionic acid). The influence of the operational factors as: feed water concentrations, feed temperatures, permeate pressures and propionic acid concentration in the feed was experimentally investigated. The binary experiments water/1-propanol was performed at feed concentrations of 5-20 wt-% water. Permeate fluxes increase when the feed water concentrations increase. The effect of temperature was studied in the range of 60-80° C, and the results show that increasing temperature leads to high values of fluxes. Experiments at two different feed pressure, 15 and 40 mbar, at the same feed concentrations and temperatures were performed to analyze the influence of permeate pressure on the permeate fluxes. It was observed that total fluxes and selectivity are higher at lower permeate pressures.

Ternary mixtures experiments with different concentrations of propionic acid in the feed (10-45 wt-%) were performed and the results were compared with the corresponding binary mixtures experiments. The permeate fluxes of the ternary experiments water/1-propanol/propionic acid are comparable with the results from the binary mixtures water/1-propanol but are considerable smaller compared with binary mixtures water/propionic acid. Also, high amounts of propionic acid permeate through the membrane. After these tests it is concluded that propionic acid changes the performance of the membrane by increasing permeates fluxes and decreasing the selectivity. Therefore is recommended to work at very low concentrations of propionic acid in the feed for an efficient separation with this pervaporation membrane.

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