

Methanol separation from organics by pervaporation with modified silica membranes

H.M. van Veen

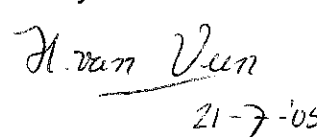
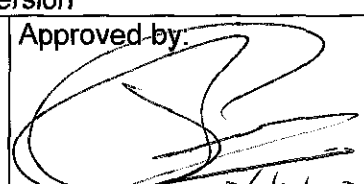
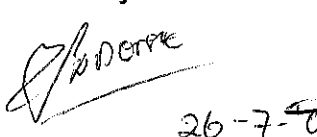
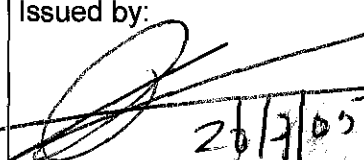
Y.C van Delft

B. Bongers

C.W.R. Engelen

P.P.A.C. Pex

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Abstract

Microporous methylated silica membranes have been made and tested up to a size of 1 m² of membrane area and they can be used for the separation of methanol from organics. Measurements have shown that fluxes are much higher than for polymeric membranes with good selectivities and that the membranes can be used up to at least 125°C. Economic calculations have shown that these inorganic pervaporation membranes can very well replace existing - distillation based - processes.

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1. Introduction

Microporous silica and zeolite membranes are being developed for the separation of water from organic process streams by pervaporation [1,2]. They can be used in hydrogen separation processes as well. By incorporating methyl groups in the silica membrane structure, the steam stability of these membranes in gas separation applications and water stability in pervaporation can be improved [3, 4, 5]. Recently we have found that these modified silica membranes can also be used in the separation of methanol from organics by pervaporation. In this paper measurement results for the separation of methanol from THF, toluene, MTBE and several alcohols will be presented and the technical and economic potential of the new pervaporation membranes will be evaluated and compared with conventional distillation based processes by chemical engineering and flow sheeting (ASPEN+) calculations. Results of the separation of methanol from MTBE will be shown up to a scale of 1 m² of membrane area. The aim of using these membranes is to increase the capacity of an existing process, to reduce the energy consumption especially compared with distillation processes and show that favourable economics are possible for the pervaporation based process.

2. Experimental

Microporous methylated silica membranes have been prepared in a tubular geometry with the membrane layer coated on the outside of the support system. The outer diameter of this tube is about 14 mm and the length of the membrane is 1 meter. In general these membranes have a good quality in pervaporation as the preparation procedure and defect control have been optimised even up to this larger scale. These membranes have been prepared by coating intermediate alumina layers and the final silica membrane layer on top of a commercially available alumina substrate tube [5].

The membranes have been used for the separation of methanol from several organic mixtures at different temperatures and feed concentrations, using a lab scale test system that can operate up to 200°C and 40 bar feed pressure with a membrane area of about 50cm². Testing with a pilot scale test installation containing 24 membrane tubes with a length of about 1 meter (≈ 1 m² membrane area), which can operate up to 150°C and 10 bar pressure using a maximum feed liquid amount of 1000 litre has been performed as well. Analysis of the different mixtures has been done by refraction measurements and/or by gas chromatography. In all pervaporation tests the permeate pressure was set to 10 mbar.

The results of these tests have been used for a process evaluation using both spreadsheet calculations and ASPEN+ flow sheeting calculations. Both the conventional - distillation based - process and the pervaporation based process have been calculated. Detailed economic calculations will be given for the separation of methanol from toluene, while the separation of methanol from THF, MTBE and higher alcohols will first be discussed shortly.

3. Results and discussion

Results of lab scale pervaporation tests using a methylated silica membrane with an area of about 50 cm² in different binary alcohol mixtures at 45°C are presented in Table 3.1.

Table 3.1 *Lab scale pervaporation test results of the methylated silica membranes*

Mixture	MeOH feed conc. (wt.%)	Total flux (g/m ² h)	Permeability MeOH (kg/m ² hbar)	Permeate conc. MeOH (wt.%)
MeOH pure	100	1620	3.74	100
MeOH - EtOH	5	270	4.30	47
MeOH - 1-propanol	5	130	3.61	90
MeOH - n-butanol	5	150	3.34	92
MeOH - MTBE	5	370	6.41	90
MeOH - toluene	5	1230	15.50	97

From these results it is clear that methanol separation from ethanol has a low selectivity. Methanol separation from higher alcohols or organics leads to permeate concentrations of more than 90 wt.% MeOH, starting from 5 wt.% in the feed. The flux for pure methanol is much higher than for the binary mixtures as the driving force for transport is much higher and no hindrance of the second component is occurring. The MeOH flux is different in each mixture as the activity for methanol is different in each mixture. When the permeability for methanol is calculated some surprising results are obtained. This permeability is almost constant for pure methanol and methanol binary mixed with other alcohols, but for MeOH in MTBE and especially in toluene the permeability is strongly enhanced and even larger than for pure methanol. Adsorption on the membrane surface could play a role or different steps in the transport are rate limiting, e.g. evaporation, micropore transport and desorption from the pore. Finding an explanation for this effect is still part of the research in this running project, see also [6, 7].

The separation of methanol from MTBE has been studied at different temperatures, up to 125°C. For this a feed mixture containing 5 wt.% of methanol has been used. The most important results are presented in Figure 3.1. Similar results for a second membrane can be found in [6].

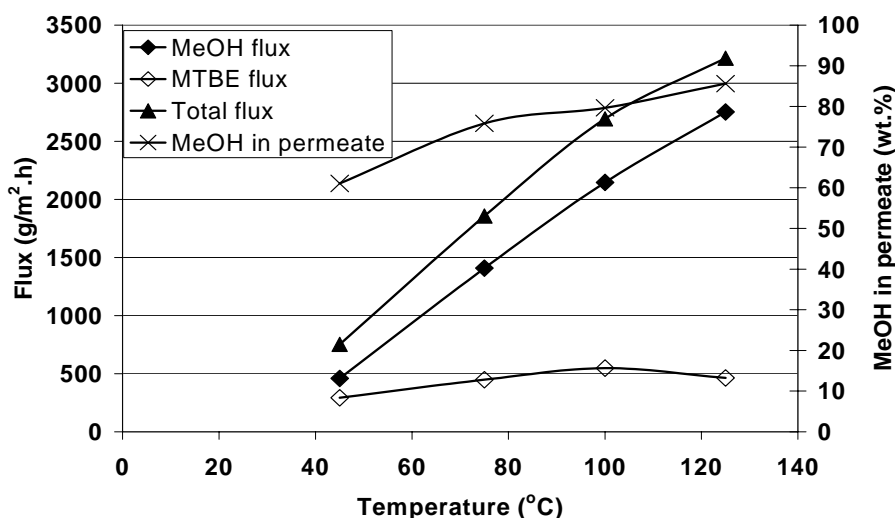


Figure 3.1 *Influence of temperature on flux and permeate purity for MeOH-MTBE*

It can be seen that the MeOH flux strongly increases with temperature as the driving force for methanol increases with temperature. The MTBE flux only varies slightly with temperature. As the membrane used here did contain some defects, the methanol concentration in the permeate is lower than for other membranes tested, compare with e.g. Table 3.1 and [6]. Long term testing at 125°C showed that the flux decreases about 50% during the first few days of continuous operation. After this the flux is stable and the membrane has been on stream for more than 125 days at 125°C. The selectivity increased somewhat during this time and the permeate contains more than 90 wt.% methanol.

As these results are very promising, measurements using a pilot scale 1 m² membrane area installation (Figure 3.2) have been performed for the MeOH-MTBE process at the location of a chemical industry and using their process mixture. The main results are presented in Figure 3.3. The results show that more than 95 wt.% MeOH in the permeate can be obtained. Furthermore, comparable to the lab scale measurements the flux strongly increases with temperature and fluxes of more than 25 kg/m²h are obtained at 95°C for a feed mixture containing 25 wt.% MeOH.



Figure 3.2 Pilot scale 1 m² membrane area pervaporation test system

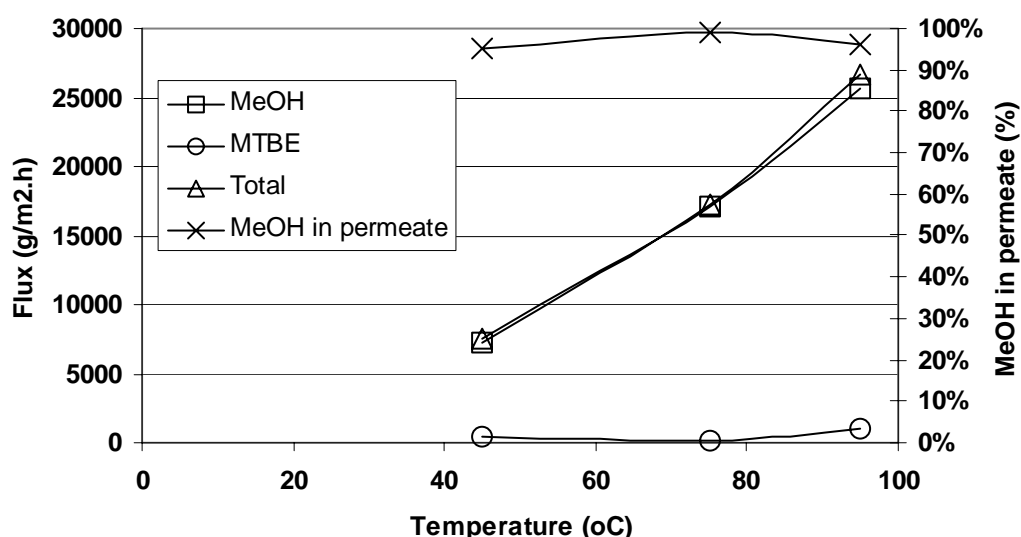


Figure 3.3 Fluxes and permeate purity for 25 wt.% MeOH in MTBE vs. temperature for a 1 m² membrane area system

Lab scale measurements have been performed at different temperatures and feed concentrations for a MeOH-toluene mixture. This has been done for evaluating the possibility of using pervaporation membranes to replace an existing MeOH-toluene separation process. In the conventional process excess of water is used in an extraction system followed by two distillation columns, see Figure 3.4. By membrane pervaporation this could be done in one step.

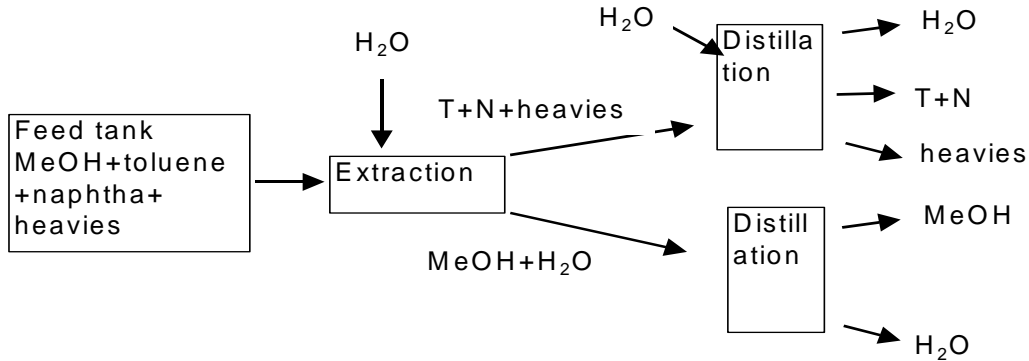


Figure 3.4 Schematic presentation of existing MeOH-toluene process

In Figure 3.5 results are presented for different feed concentrations methanol in toluene for a feed temperature of 60°C. The permeate contains almost pure MeOH and even for a feed containing 1 wt.% of methanol the permeate still contains more than 97 wt.% MeOH. The flux first increases strongly with an increase in methanol feed concentration and at about 5 wt.% in the feed it only slowly increases with the feed concentration. The reason for this is that the driving force for methanol transport based on activity and vapour pressure of methanol in toluene hardly increases anymore above 5 wt.%. When the flux is plotted against this driving force a perfectly straight line is obtained. These results have been implemented in the ASPEN+ flow-sheeting programme and for both the conventional and membrane based process the economics have been calculated. As indicated in Figure 3.6 the economics for the pervaporation process are much better than the conventional process. This is mainly caused by much lower variable operating costs as two larger energy consuming distillation columns are replaced by membranes: almost 80% of the energy can be reduced.

Similar measurements and calculations for MeOH-THF separation have indicated a cost reduction of 48% and an energy reduction of 49%.

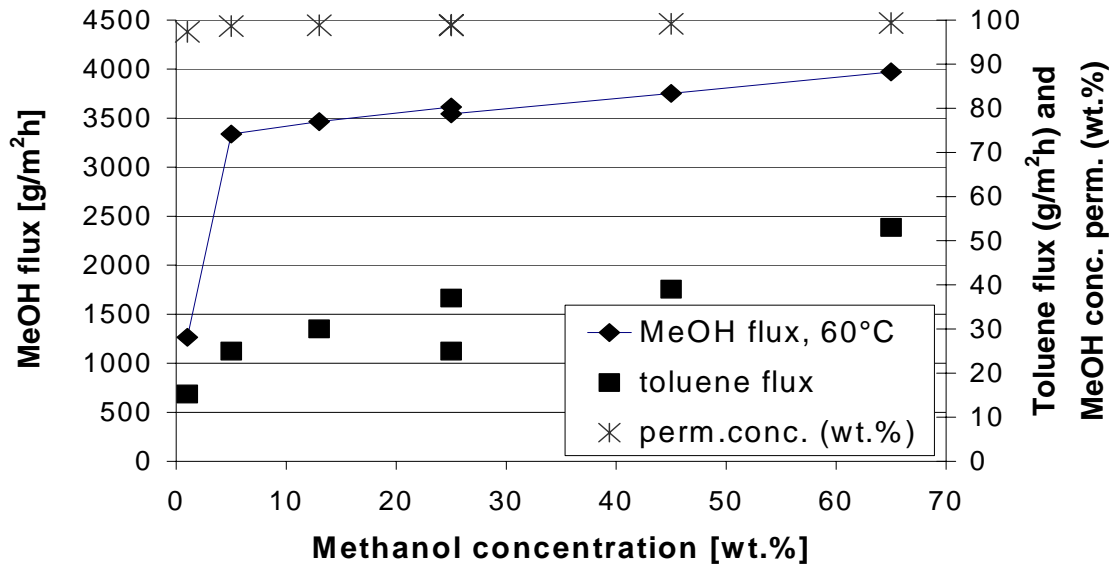


Figure 3.5 Influence of feed conc. on flux and permeate purity for MeOH-toluene

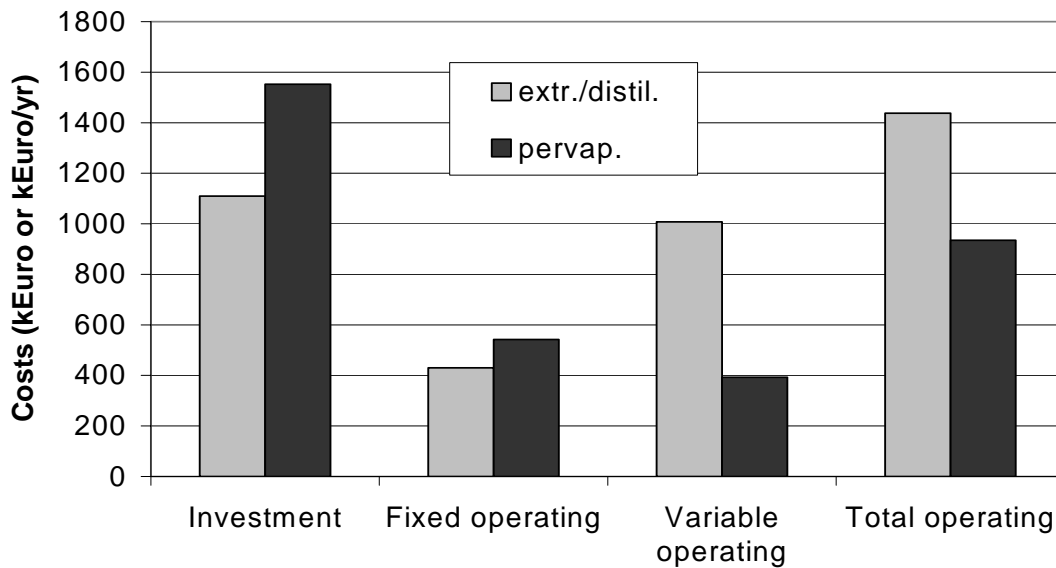


Figure 3.6 Cost comparison of conventional extraction/distillation process vs. pervaporation

4. Conclusions

Microporous methylated silica membranes have been made and tested up to a size of 1 m² of membrane area and they can be used for the separation of methanol from organics. Measurements have shown that fluxes are much higher than for polymeric membranes with good selectivities and that the membranes can be used up to at least 125°C. Economic calculations have shown that these inorganic pervaporation membranes can very well replace existing - distillation based - processes.

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