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INORGANIC MEMBRANES FOR PERVAPORATION

Proof of concept

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Acknowledgement/Preface

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Abstract

The aim of the here described project was to develop membranes, modules and systems to come to a quick implementation of tubular inorganic membranes in dewatering pervaporation processes in the process industry as a cost effective and energy efficient alternative for e.g. distillation.

Based upon commercially available ceramic support tubes microporous silica membranes for pervaporation have been made using fully automatic techniques on a commercial scale. The production facility has been designed for an output of 12,000 tubes (or about 500 m^2) annually. Dehydration of several organic mixtures using these membranes has been performed from lab scale up to a scale of 1 m^2 of membrane area and shows good selectivities and fluxes that are much higher than for polymeric membranes. Process calculations for some processes show high energy savings and favourable economics.

The silica membranes however show flux decline in time (at an almost constant selectivity) and the membrane performance has been improved by incorporating methyl groups into the silica structure. This methylated silica membrane now meets the long term flux demands as needed in industrial processes. As the silica based membrane shows a structural reorganisation at temperatures above 100^{o}C, the use is at this moment limited to this temperature. Membrane fouling due to salts in the feed mixture in combination with membrane cleaning is a topic for further research.

An isothermal module for the inorganic pervaporation membranes has been developed and optimised by chemical engineering and computational fluid dynamics calculations towards heat transfer and pressure drop. Also costs for membrane systems have been optimised by smart module arrangements in a pervaporation set-up. Modules up to 5 m^2 and designs for larger scale modules have been made.

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EXECUTIVE PUBLISHABLE SUMMARY

Objectives and problems to be solved

The objective of the project was to develop membranes, modules and systems to come to a quick implementation of tubular inorganic membranes in dewatering pervaporation processes in the process industry as a cost effective and energy efficient alternative for e.g. distillation. By extensive pilot scale on-site testing it was intended to show that considerable (50%) increase in energy efficiency can be obtained, and purer products, thus higher product quality can be achieved. Furthermore throughput can be increased leading to cheaper production. Simplified (downstream) and/or novel processes can be made. Because of the avoidance of entrainers in azeotrope breaking less organic wastes will be obtained and organic emissions are reduced through recycling of solvents and as a consequence less transport of chemicals (safety) is needed. Finally less emission of CO_2 SO_2 and NO_x will occur. This novel technology will strengthen the European competitive position, as it is the first time this technology becomes available on (semi-) commercial scale world-wide.

Description of work

The work concerns the proof of concept of this energy efficient inorganic membrane pervaporation technology in organic solvent dewatering applications and in the production of esters or resins wherein the equilibrium is shifted by the removal of water as reaction product. The applications are representative for a large group of processes. Practically the work comprised experimental laboratory research, bench-scale studies and extensive pilot testing with real process feeds using a pilot module (1m^2), which has been developed. The latter is providing the technical operating window of the technology. The module has been hydrodynamically optimised with respect to heat and mass transfer and contains low-cost and robust tubular silica pervaporation membranes for which the production technology has been developed in the project. Finally a semi-industrial pervaporation module (about 5 m^2 membrane area) including all aspects of a full-scale module has been made and functionally tested. The work was guided and supported by process system studies (flow sheeting) and mechanical and chemical engineering studies. Aspects such as membrane performance (flux, selectivity), durability, and full-scale chemical process pre-designs have been covered. Finally detailed technical, economic issues and energy efficiencies as compared to conventional options have been addressed.

The consortium brought together expertise on inorganic membrane, module and system manufacturing, detailed knowledge of both existing (conventional) and pervaporation separation processes, and process and implementation know-how for the relevant sectors. This project is the bridge to the final implementation of the inorganic membranes for pervaporation into the market.

Results

The recipes and technology of preparing the microporous silica membranes for pervaporation have been scaled up. The commercially available ceramic substrate tube from TAMI has been selected as commodity support and membrane coatings have been applied successfully onto these substrates, both on lab scale and with the fully automised installation at Sulzer. These commercially produced membranes have a good performance in pervaporation and show similar results as the membranes prepared on lab scale. Some debugging of the full-scale coating procedure is, however, still needed. The production capacity of the membrane manufacturing system and the peripherical manipulation has been designed for an output of 12,000 membrane tubes annually.

Lab scale pervaporation testing of the membranes has been performed using several feed mixtures. In general the membranes perform very well in dehydration. The fluxes are much higher than reported for polymeric membranes and the water purity of the permeate meets the demands. The dewatering of tertiary butyl alcohol, A-fuel and propylene glycol have been selected as processes to be tested with a skid mounted unit of 1 m^2 membrane area scale. These processes have first been tested extensively on lab scale and show good results for both flux and selectivity. First calculations also indicate favourable economics. Larger scale testing of these processes using a 1 m^2 membrane area test installation based upon inorganic membranes has shown that dewatering of A-fuel on pilot scale even leads to higher selectivities than on lab scale: good fluxes were combined with more than 90 wt.% water in the permeate. For the A-fuel mixture on pilot scale fouling of the membranes occurred due to deposition of minerals from the tap water used. Lab scale testing has shown that this fouling does not occur in vapour permeation, though the selectivity in vapour permeation is somewhat lower than for pervaporation. In the propylene glycol mixture testing the selectivity of the membrane in 1 m^2 testing was lower than as measured on lab scale (very high selectivities), due to some defects in the membranes. For A-fuel and propylene glycol dewatering energy savings are respectively 60% and 36%. For the TBA process the price increase for the TBA product due to the use of the pervaporation membranes is 3.5€ per ton of TBA sold, which is less than the daily fluctuations of the market price. For A-fuel the economics of the process are not favourable. For the glycol production process the investment in the membranes will be paid off by the capacity increase within one year. As a reference process dehydration of iso propyl alcohol was investigated and for this process investment operation costs are reduced by more than 40% and energy savings up to 85% could be achieved for pervaporation compared with a conventional distillation process. Furthermore the process of producing lactic acid has been optimised by incorporating inorganic dewatering membranes.

During testing the silica membranes a water flux decline of about 50% in the first few days was observed in combination with a further slow decline of the flux over a longer time period. This was also found in literature, however no solution for this problem was indicated there. Improvement of the stability of the silica membrane was necessary in order to have a membrane that is as widely applicable as possible. By incorporating methyl groups in the silica structure the initial flux decline has almost disappeared and the methylated silica membranes almost meet the first set of criteria for long-term industrial implementation. The membranes can, for the moment, only be used in dewatering up to a temperature of 100°C as at higher temperatures (e.g. 165°C) the membrane looses its selectivity after less than 50 days of continuous pervaporation testing. Also the stability in more aggressive environments is still to be improved.

Calculations on heat transfer in a membrane module that operates isothermally and pressure drop on the feed side have been combined with calculations on module arrangements. Optimisations for module arrangements in combination with the processes have been developed. These have been combined with cost optimisations of a membrane system as a function this arrangement, which showed that the membrane costs are much higher than the feed pump costs. Thus it appears that modules in series in general lead to lower costs than modules (partly) arranged in parallel. Furthermore it was shown with heat transfer calculations that steam heating of the isothermal silica membrane system (SMS®) module is much more efficient than using thermal oil for heating. Based upon chemical engineering and computational fluid dynamics calculations the pressure drop of the SMS® membrane module has been minimised. Several modules (single tube, two membranes, up to a module with 5 m^2 of membrane area) have been made and designs for larger scale modules are available.

Exploitation

The results will be implemented on a larger (pilot plant) scale. End-users from the (petro)chemical, oleochemical and pharmaceutical industries have major interest in up-scaling and using the technology on full scale in their processes. Furthermore they aim at the development of new chemicals and advanced process-routes using the results of this project. From the hardware point of view (membranes and modules) a manufacturing plant is in the start up phase. Selling membranes, modules, and systems for application in separation processes in applications fields as wide as possible has started as well. Because of the project results the membrane producer and membrane system developer Sulzer Chemtech will world-wide be the first company that commercially produces microporous silica membranes for dewatering that have proven to work under different processes. A client has placed a first order for a solvent dehydration plant into which several 10 m^2 modules have been installed. The respective pervaporation plant shows a very simple design, as the feed side piping is reduced to a simple connection of the modules.

1. OBJECTIVES AND STRATEGIC ASPECTS OF THE PROJECT

1.1 Socio-economic objectives and strategic aspects

Chemical feedstocks, solvents and products of (chemical) reactions in the liquid phase are often a complex mixture of organic components and in many cases water. These mixtures are difficult to separate. The separation is mostly performed by various distillation techniques sometimes combined with the use of chemicals (entrainers), which can be dangerous substances and/or hazardous to the environment. Distillation is an energy consuming process mainly due to the need to evaporate liquid and for generating reflux in addition to the liquid taken off at the column head as top product. These process conditions are widely used in the separation of mixtures containing many components with narrow boiling points, where for several reasons the reflux stream can be far bigger than the final product stream and in the separation of azeotropes, where multiple-step distillation including entrainers are required.

Pervaporation is the selective evaporation (permeation) of only one component of a liquid stream by means of a membrane, which is in direct contact with the liquid mixture. Energy use in dewatering by pervaporation depends primarily on the amount of water to be removed, because only water has to be evaporated. Even difficult separations like azeotropic mixtures can be performed in one step. Energy savings compared to distillation can amount to as much as 90%. In addition this technology can be used to combine reaction and separation steps leading to very energy efficient process intensification (e.g. in esterifications). Thus, pervaporation is very innovative and will have important benefits: i) considerable energy efficiency increase ii) purer products, thus higher product quality; iii) increased throughput, thus cheaper production; iv) simplified (downstream) and/or novel processes; v) less organic wastes and organic emissions through recycling of solvents and as a consequence less transport of chemicals (safety); vi) avoidance of the use of entrainers in azeotrope breaking; vii) less emissions of CO_2 SO_2 and NO_x.

Pervaporation has been developed with polymeric membranes and they have been tested in several applications. However, the limited stability - mainly low temperature and mechanical stability - of the polymeric membrane materials under process conditions is the main reason why pervaporation has not been able to replace distillation on a large scale and the progress of this technology is slow. These problems can be solved by using inorganic membranes, which are mechanically robust, resistant to aggressive organic solvents and can withstand temperatures up to at least 250 °C.

The main objective of this project is to further develop inorganic membrane pervaporation technology, which will reduce the energy needed for separation in chemical and related - production processes by more than 50%. Furthermore to improve the process-efficiency and to reduce the use of hazardous chemicals, by introducing this technology as a replacement for the energy intensive and often environmentally harmful (azeotropic) distillation with entrainers. The technique of inorganic membrane pervaporation will be brought up to semi-industrial scale by advanced scientific and technical development within a trans-national consortium and Europe will have a very strong competitive position in a technology world-wide applicable and with strong global impact. Membrane producers, equipment manufacturers, process developers and chemical industry will benefit from this project, which fits perfectly in the goals of the EU policy needs.

1.2 Scientific and technical objectives

A summary of the specific scientific and technological objectives for the whole project period is given in the next table.

Table 1.1 *Objectives for the project*

Work package number	WP sub number	Objectives
1	1.1	Chose a dewatering and an esterification process for further study
	1.1	Give an overview of the existing (state of the art) processes including flowsheet development
	1.2	Insight into the efficiency of the existing processes
	1.2	Set-up for the new pervaporation process
	1.3	Optimisation of the chosen pervaporation processes
	1.4	Process evaluation and detailed economic and energy saving calculations
2	2.1	Optimise modules by chemical engineering and computational fluid dynamics
	2.1	List module and system specifications
	2.1	Engineered design of a 1 m^2 module and system
	2.2	Build and test the semi-industrial module, deliverable 8
3	3.1	Modify available test facilities
	3.1	Lab scale testing under relevant conditions and report this as deliverable 6a
	3.2	Industrial scale pilot testing on location of end-user Lyondell and report as deliverable 6b
	3.3	Functional testing of semi-industrial scale module and report as deliverable 9
4	4.1	Manufacture silica membranes for testing and for the 1 m^2 module
	4.1	Improve stability of silica membranes
	4.2	Screening and choice of available commodity supports
	4.3	Coating of commodity supports and testing, including delivery of membranes as deliverable 7 and cost effective and robust supports as deliverable 10
5	5.1	Guide and manage the project, reporting
	5.2	Technology implementation plan

2. SCIENTIFIC AND TECHNICAL DESCRIPTION OF THE RESULTS

2.1 Introduction

At the start of the project end-user Haltermann was involved in the project. The applications chosen should be of interest to them and should be representative for a large group of similar solvents/applications. The dewatering process should be a high temperature and difficult separation of e.g. aprotic solvents. The next applications were chosen as reference process for dewatering or production of:

- THF (tetra hydro furan),
- DMF (dimethyl formamid),
- DMAc (Dimethyl acetic amide),
- Ethylene diamine,
- Triethyl amine,
- EtOH + lactic acid -> Ethyl lactate.

The dewatering of PrME, DMF, and IPA (iso-propanol as a reference) have been chosen as processes for further study. The production of ethyl lactate and an ester are chosen as esterification process.

As end-user Haltermann has withdrawn from the project and Lyondell Chemical has offered their facilities to the process testing in the project, new processes that deal with water separation have been chosen for testing and process evaluation:

1. Crude TBA. The crude TBA contains a certain amount of water, which should be reduced to Lyondell specifications. The exact specifications on the purity depend on the market. The advantages of using pervaporation are a higher product price and less steam use.
2. A-fuel, which contains a lot of water, which should be reduced to increase the caloric value of this fuel to obtain a gain in market price, and to decrease the load to the waste water treatment, thereby earning money.
3. A mixture of mono-, di-, and tri propylene glycol, which in the crude form contain a lot of water. For capacity increase of the existing multiple step distillation process a feed containing a certain percentage of water should be reduced to low water content.

Besides these processes the dewatering of IPA and the production of ethyl lactate have been studied in more detail. All these five processes will be discussed further in this report.

Based upon the pilot scale testing on side at Lyondell and the lab scale experiments performed by ECN and IVT Aachen on the three process of Lyondell mentioned above, a comparison of performance and a simulation of needed membrane area has been made. The membrane characteristics have been implemented in an ASPEN User-routine provided by the IVT for the calculation of pervaporation and vapour permeation with the simulation program ASPEN Plus®. With these calculations design data for the required membrane area have been obtained. Both TBA and A-fuel separations have been calculated for the isothermal operation with the SMS® module. Since membrane costs have the major impact on the total costs of an inorganic pervaporation plant a cost estimate can be based on these as a first approximation. For all these process streams an economical evaluation has been performed.

2.2 Work package 1 System integration studies

2.2.1 Aim

Evaluate existing pervaporation processes, identify deficiencies of existing membranes, and specify the potential application of inorganic membranes. Get insight into the feasibility, energy efficiency and economics of the chosen processes comprising inorganic pervaporation membranes vs. conventional production/separation processes. Give input of information and data into testing and design. Main results: overview of the total system efficiency in terms of energy use, technical possibilities and cost-effectiveness of the pervaporation processes.

2.2.2 IPA production process

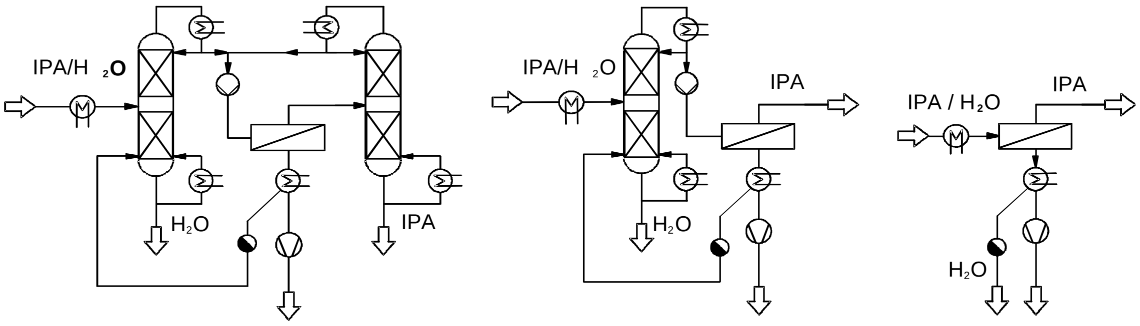
Today, the standard process for IPA/water separation is extractive distillation. Process data for this conventional process to be compared with the membrane-based process were taken from a real plant running in the German chemical industry. The IPA/water feed mixture (30 wt.% IPA) is nearly concentrated up to the azeotrope in a first column. The stream, which is removed from the top has 86 wt.% IPA. At the bottom the lower volatile component water is drawn off with a concentration of 99.99 wt.%. In the second column the breaking of the azeotrope occurs. Therefore auxiliary ethylene glycol (EG) is added almost on top to extract the water. At the top the product IPA is gained with a purity of 99.9 wt.%. At the bottom a mixture of ethylene glycol and water (95 wt.% EG) is withdrawn. In the third column the EG/water separation takes place to recycle the auxiliary to the second column.

The price for the produced IPA is about 500 €/t. The specific energy requirement for the conventional IPA/water separation is roughly 45 € per ton product. The shares are: cooling water 16.4%, 4 bar steam 25.2%, 16 bar steam 57% and electricity 1.3%. This means that for the dewatering of 1 kg IPA containing 20 wt.% water to a purity of 99,9% with extractive distillation 3.3 kWh are necessary. The investment and running costs have been taken from an existing extractive distillation plant running in a German chemical company for dewatering of IPA.

For the separation of a binary mixture of IPA and water, three competing alternatives have been identified which are shown in Figure 2.1. Coarse splitting of the azeotrope with the membrane unit installed between two distillation columns (A, left) and purification of the azeotropic distillate stream up to the desired product quality (B, centre) are the two hybrid process options, while the third is a stand-alone pervaporation membrane process (C, right).

The optimisation of the system was carried out on an economic basis including investment and running costs. The total separation costs of the extractive distillation are 84.06 €/t. The most efficient membrane configuration, option B with ceramic membranes, is with 48.18 €/t about 42.7% cheaper than the conventional option (see Figure 2.2). The stand alone process C based upon silica membranes is with 57.63 €/t more expensive than hybrid process B, because more membrane area is needed to achieve the product specification, but it is still about 31.4 % cheaper than the conventional process. Option A with the membrane unit between the two distillation columns is with 60.13 €/t and savings of 28.5% in the same order of magnitude with a slightly cheaper membrane part and a more expensive distillation due to an extra column.

The best configuration is the purification of the azeotropic distillate stream of the column up to the desired product quality. Investment and operation cost could be reduced by more than 40 % and energy savings up to 85% could be demonstrated. This compares with 2 PJ/year energy savings for Europe when the reference plant is taken as a reference for the total production in Europe. As a matter of fact the chosen base case plant is one of the least energy efficient plants in Europe and when a more efficient plant is chosen as a base case then the energy savings in the EU for IPA production would be about 0.3 PJ/year.



(A) (B) (C)

Figure 2.1 *Pervaporation for azeotrope splitting between two distillation columns (A, left), separation up to the product specification (B, centre) or as stand-alone process (C, right)*

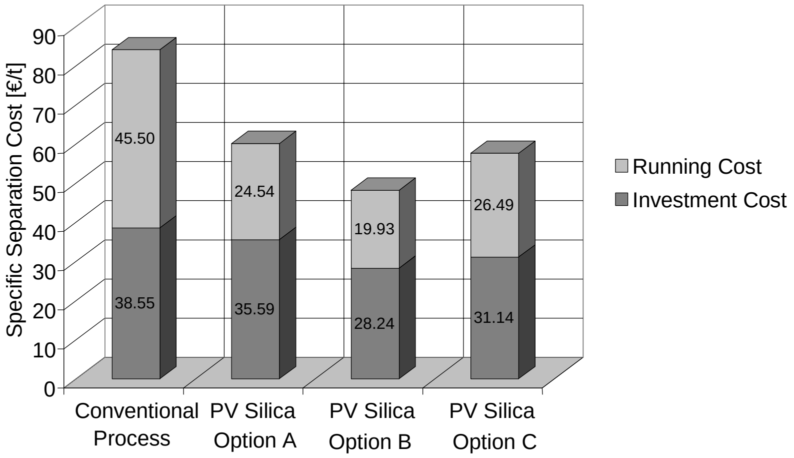


Figure 2.2 *Comparison of conventional extractive distillation with the three process options with silica membranes in terms of capital and operation cost*

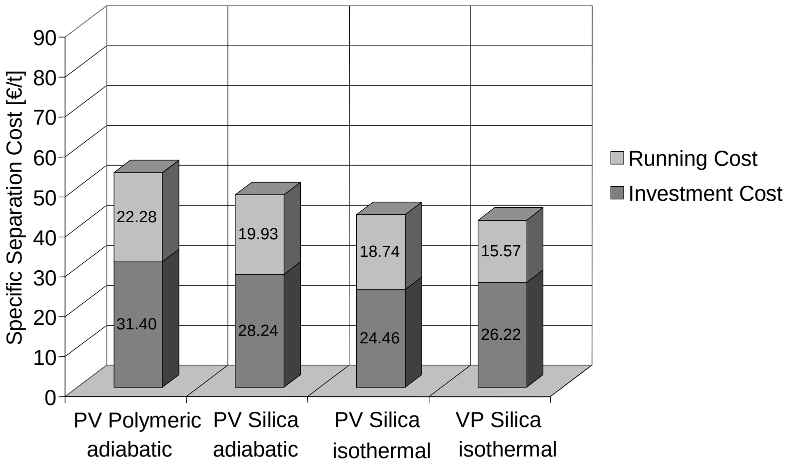


Figure 2.3 *Evaluation of different membranes (PVA/PAN and silica) and operation modes (adiabatic and isothermal pervaporation and vapour permeation) in the same system configuration in terms of investment and operation cost*

The economical comparison of the different membranes and operation modes in the same system design is illustrated in Figure 2.3. Inorganic membranes allow 11 % lower total separation cost in comparison to polymeric materials. Among the membrane based options vapour permeation combined with distillation should be preferred over isothermal pervaporation. Adiabatic pervaporation is the most expensive. Additionally, the use of polymeric and ceramic membranes in standard adiabatic pervaporation, isothermal pervaporation with Pervap® SMS modules and vapour permeation with silica membranes has been evaluated for the best process configuration B.

2.2.3 Ethyl lactate production process

Ethyl lactate is a so-called 'green solvent' as it is produced from biomaterials and it is easily biodegradable. It is fully miscible with water, and a very potent solvent, which can replace aliphatic, aromatic, and halogenated hydrocarbons in many applications, e.g. in cleaning, degreasing, lacquers, and paints. Raw materials, ethanol and lactic acid can be produced from agricultural products, especially sugar and starch containing materials, by fermentation processes. Today, ethyl lactate is already produced in considerable amounts, and it is predicted that this production will increase in the next future if production costs can be reduced. Lactic acid and lactates, purified via ethyl lactate, can be polymerised and converted into biodegradable plastics from which packing materials and fibres for clothing can be produced.

In the conventional production process of today raw lactic acid and a surplus of ethanol are mixed and reacted close to the equilibrium in either batch or continuous reactors. Even with a surplus of ethanol a considerable amount of lactic acid remains unreacted and additional water is introduced into the reactor with the azeotropic ethanol. The reaction mixture is separated in several stages, first distilled under vacuum, in order to remove the unreacted lactic acid. Then ethyl lactate is separated from water and the surplus alcohol, and purified by an additional vacuum distillation step. Finally the ethanol is separated from the water formed in the reaction, and returned to the reactor. In the first distillation due to the presence of water partial hydrolysis of the ethyl lactate occurs, polluting the ethyl lactate with lactic acid and requiring an additional purification step. Some ester is transferred to the last distillation column, too, where it is hydrolysed, leading to severe corrosion problems, as lactic acid is a fairly strong and corrosive acid.

When pervaporation/vapour permeation is coupled with the esterification reaction a scheme as shown in Figure 2.4 becomes feasible.

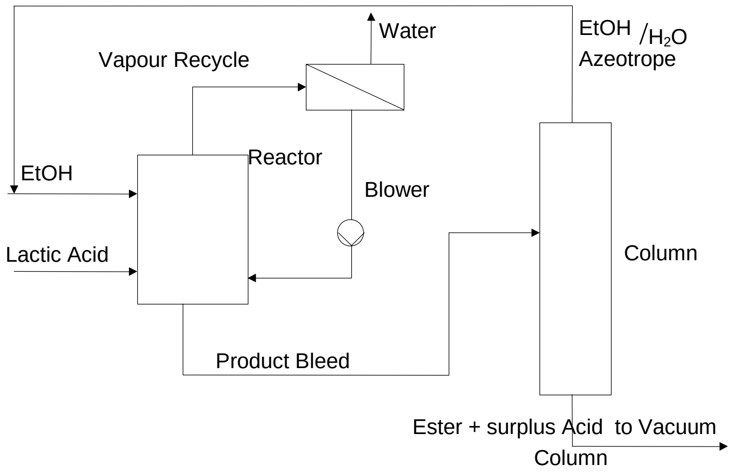


Figure 2.4 *Continuous ethyl lactate process, reaction coupled with vapour permeation*

Here lactic acid and rectified ethanol are fed continuously to a reactor in such a way that a sufficient large surplus of ethanol exists under stationary conditions. The vapour phase over the liquid reaction mixture is passed over a membrane system, which operates at the same temperature as the reactor, at 125 to 145° C, and is then returned to the reactor by means of a blower. The water formed in the reaction, and that portion introduced with the rectified alcohol which is consumed in the reaction, is extracted through the membrane and the water content in the reactor is kept at a level, which is equivalent to the composition of the ethanol - water azeotrope, with respect to the surplus ethanol. A bleed stream comprising ethyl lactate, a minor portion of unreacted lactic acid, mostly in the form of the dimer, and the ethanol - water azeotrope is extracted from the reactor. In a first distillation column this stream is separated into ethyl lactate and unreacted lactic acid at the bottom, which is separated in a second vacuum column into the pure ester and the acid. The water- ethanol azeotrope from the top of the first column is returned to the reactor.

This scheme requires pervaporation/vapour permeation membranes, which can be operated at elevated temperature, thus only ceramic membrane are applicable. As water is directly removed from the reaction mixture the reaction equilibrium is shifted towards the wanted product, and, depending on the surplus of ethanol up to 97.5% conversion of the acid can be obtained. In the purification of the ethyl lactate no water is present, thus no hydrolysis of ester can occur. Besides an improved volume - time yield for a given reactor and a high conversion of the acid the new process needs less energy for the downstream product purification, and reduces the corrosive attack on the equipment.

Simulation of this esterification process including the continuous removal of water from the reaction mixture leads to valuable information on these investment and operation costs. From these data a comparison with the equipment of state-of art installation can be performed and the potential cost reduction for both investment and operation can at least be estimated. Even sensitivity analysis, changing reaction temperature and membrane performance data, and at least to a certain extend, membrane costs, can be performed.

2.2.4 Optimisation of Lyondell's TBA process

The TBA process has been calculated for adiabatic module operation (10 m² per module with a following interstage reheating of the retentate up to the initial temperature) and for the isothermal operation with the SMS® module. The benefit of dewatering TBA is based on the product improvement and with it a higher achievable product price. For dewatering of TBA at a feed temperature of 105°C requires a membrane area of 180 m². The total costs can be approximated to about be 0.53 Mio €. Prorating the costs on the production of 6 t_{TBA}/h for 3 years the minimum excess profit per ton of TBA sold is less than the daily fluctuations of the market price.

2.2.5 Increase of the caloric value of A-fuel from Lyondell

The A-fuel process has been calculated for adiabatic module operation (10 m² per module with a following interstage reheating of the retentate up to the initial temperature) and for the isothermal operation with the SMS® module. For A-Fuel at a feed temperature of 100°C a membrane area of 150 m² is needed for the adiabatic mode while for the isothermal mode only an area of 115 m² is needed. The cash benefit of dehydrating the process stream can be found in the increased calorific value of the product, which is 21.215 MJ/kg for the feed and at least 27.660 MJ/kg for the product after membrane treatment.

The lab and pilot scale permeate quality is very similar whereas the pilot scale water permeate fluxes are significantly lower by a factor of 1.5-2 than those measured in lab scale. Due to the lower membrane performance in the pilot testing the final membrane area needed for dewatering the A-Fuel increased from 140 m² to 260 m². Assuming a membrane price of 3000 €/m², the plant would exceed the cost limit. Thereby an increase of the flux or a decrease of the membrane prices of about 40% is necessary to reach an economic viable process based upon membranes.

In the A-fuel process the water amount has to be reduced to a lower water content. When this has to be done by distillation the main energy use will be in the reboiler duty. Assumed now is that for distillation the reboiler duty is 4,65MJ/kg. The energy use in distillation is 186 TJ/year. Based upon water evaporation in pervaporation, the condensing energy of the permeate and the heat needed for isothermal operation of the membrane module a total energy use in PV of 76 TJ/year is needed. This would lead to an energy saving of pervaporation compared with distillation of 110 TJ/year or 60% reduction.

2.2.6 Propylene glycol production increase for Lyondell processes

For the propylene glycol process the amount of water in the feed is to be reduced either by distillation or pervaporation. The energy uses are respectively 50 TJ/year and 32 TJ/year. The energy saving on year basis is 18 TJ or 36%. Costs savings based upon the use of natural gas as heat source would be about 77 k€ per year. The investment costs that are needed for this process (510 m^2 of membrane area) are about 1.5 M€. This would lead to almost a doubling of the capacity of the glycol mixture or an increase in income of 69 M€/year. For a return on investment within 1 year this would mean that the net profit by Lyondell would have to be 2.2% of the extra income to pay off the membrane installation within 1 year. This is very well possible.

2.3 Work package 2 System engineering and development

2.3.1 Aim

To engineer, design, and construct the pilot scale (1 m^2) membrane modules and the rigs, which are going to be used for on-site testing and to build the semi-industrial scale membrane module. Model the performance of the module under industrial conditions and compare to calculations. Use the data and experience from the pilot module for up scaling to an industrial size module. Main results: 1 m^2 pilot scale pervaporation installations and a semi-industrial scale (5 m^2) inorganic membrane pervaporation module.

2.3.2 Test installations

Several lab scale pervaporation and vapour permeation test installations have been build and used by the project partners. A flow sheet of a high temperature and high pressure (180°C, 40 bar, feed vessel holds a volume of up to 40 l) laboratory test plant is given in made.

A so-called skid mounted pervaporation unit has been designed and built by Sulzer Chemtech for pilot scale testing of the ceramic membranes. The SMS®-module based upon the not-yet optimised module concept incorporating the membranes has been designed and built by ECN, see Figure 2.5. The membrane module contains 24 microporous silica membrane tubes with a length of 91 cm and it has a membrane surface area of about 1 m^2. This skid unit has been used for on-site testing at Lyondell.

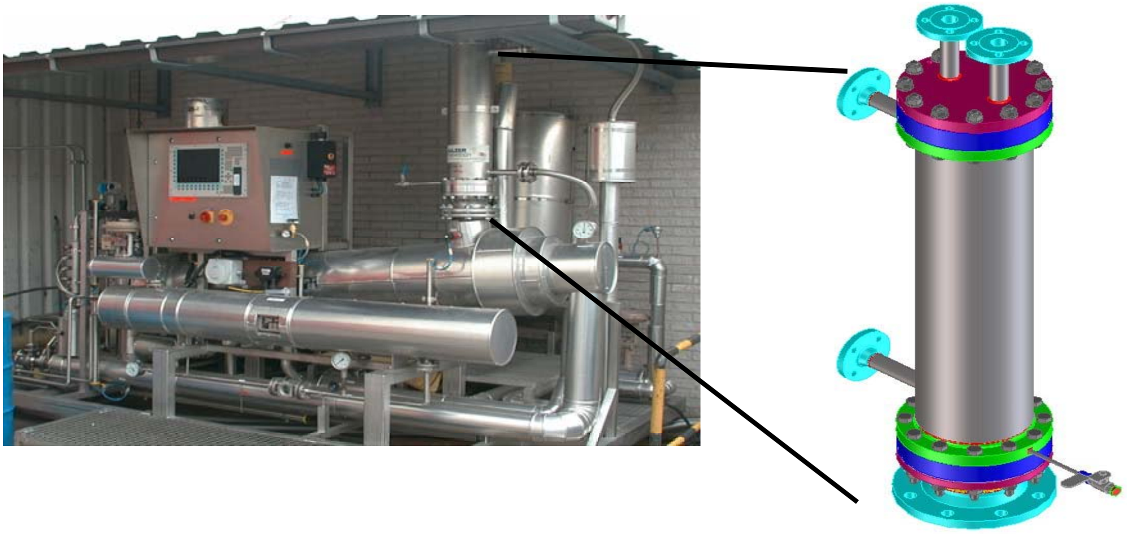
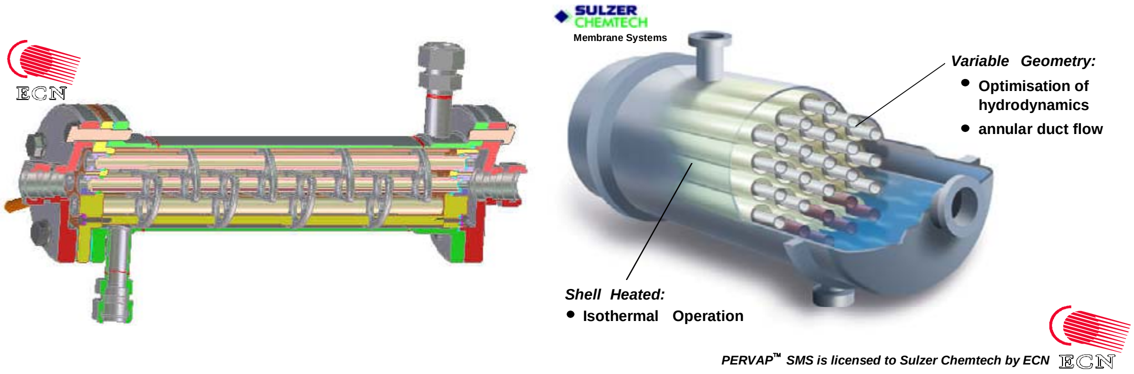


Figure 2.5 *1 m^2 skid mounted unit including module drawing*

2.3.3 Module calculations and optimisation

Based upon the above mentioned criteria two different module concepts (presented in Figure 2.6) with inorganic, tubular membranes on industrial scale have been made and modelled with chemical engineering calculations. The first geometry investigated was the baffled tube-and-shell concept with shell-side feed. The second one is the new isothermal tube-in-tube concept (SMS®-module) with feed flowing basically in series of annular ducts. For both modules ECN and Sulzer made a basic concept. IVT Aachen has optimised the SMS® concept using chemical engineering modelling using a spreadsheet in MS-EXCEL® and Computational Fluid Dynamics.



Tube & Shell Design

SMS- Concept
(annular duct_

Figure 2.6 *The two developed module concepts*

Details on the SMS® module optimisations performed will be presented below. These comprise:

- the pressure drop on the feed side of the module,
- concentration and temperature profiles on the feed side,
- heat transfer on the feed side,
- module arrangement, and,
- final design.

Feed side pressure drop

Especially feed pressure drop is an important issue of the module design in the SMS®-concept. The overall drop is dominated by the annuli, the deflection and additional feed installation like membrane fixings. The computed pressure drop for two different feed gap geometries as function of the velocity is presented in Figure 2.7. Momentum resistance in the feed turns (deflection plates) is more complex and gains increased importance due to the multi-pass operation. CFD-work will give excellent information on this item. The CFD-activities comprise the items: influence of end-caps and influence of spring assembly.

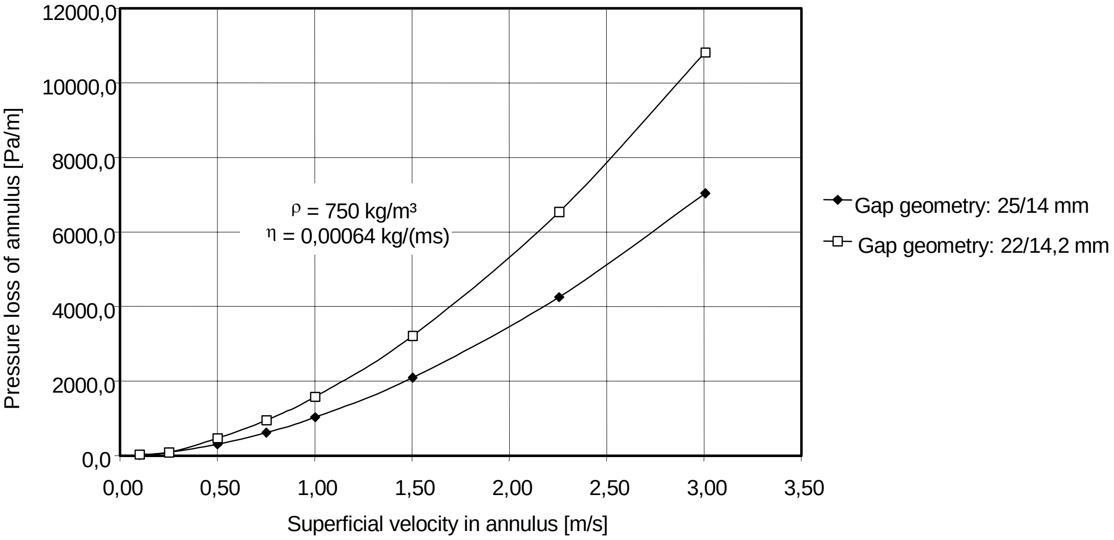


Figure 2.7 *Computed specific pressure drop of the annulus with CEC*

The membrane tubes are covered with different metal caps at both ends. These caps have a larger diameter than the membrane itself and they are partly located in the feed flow e.g. in the deflection channel. Therefore these caps might increase the overall pressure drop. The pressure drop of the spring clamps is an addition of the effect of the two end caps and the two springs. The cruciformed springs further reduce the free flow area and increase strongly the acceleration of the feed and consequently the pressure loss. Summarising, this leads to an extremely high overall pressure drop over the spring assembly.

Concentration and temperature profiles on the feed side

CFD calculations offer the opportunity to simulate the efficiency of the membrane module by visualising the flow pattern in combination with the temperature and concentration gradient as a consequence of heat and mass transfer at the walls. In Figure 2.8 and Figure 2.9 examples of the results can be seen.

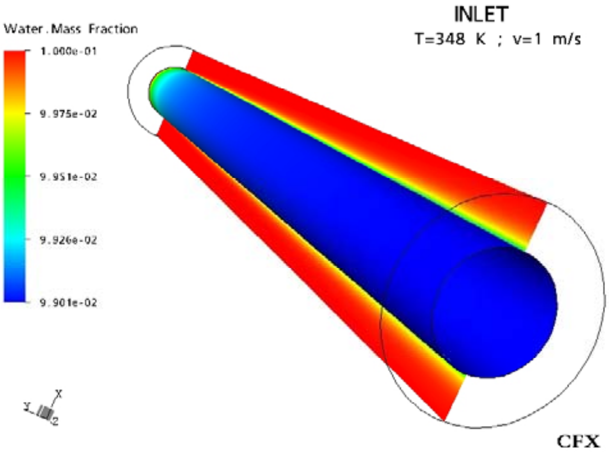


Figure 2.8 *Simulation of a concentration and temperature dependent permeate flux at 0.2 m membrane wall causing the mass fraction gradient within the annular duct and at the membrane wall*

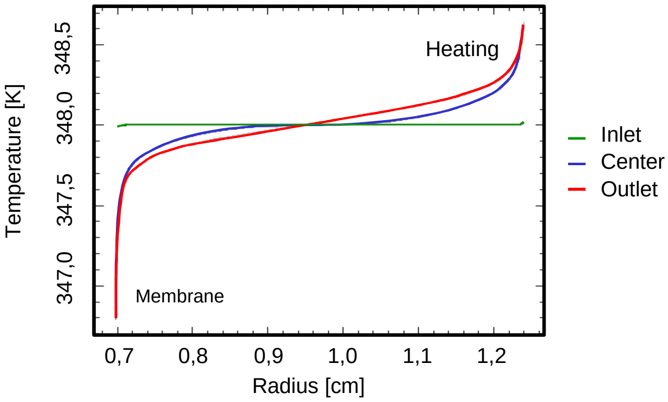


Figure 2.9 *Temperature profile in the annular gap (membrane radius 0.7 cm, radius heating wall 1.25 cm) perpendicular to the membrane at the inlet, centre and outlet of a 0.2 m tubular membrane*

The selective flux over the tubular membrane wall causes the concentration gradient in the annular duct (Figure 2.8). The lowest water concentration in the system is observed at the membrane surface as expected. This still simple geometry can now be extended to the complete 3 dimensional module with baffles and deflections.

The temperature profile in the annular duct perpendicular from the active membrane layer (0.7 cm) to the heating wall (1.25 cm) is shown in Figure 2.9. The CFD simulations compare very well with experimental data on a ‘semi-isothermal’ module for the dehydration of iso-propanol at 100°C.

Comparing the simulated results of the water flux with the experimental data (Figure 2.10) for the dehydration of isopropanol at 100°C a very good agreement is observed. Only the water flux is implemented into the simulation set-up.

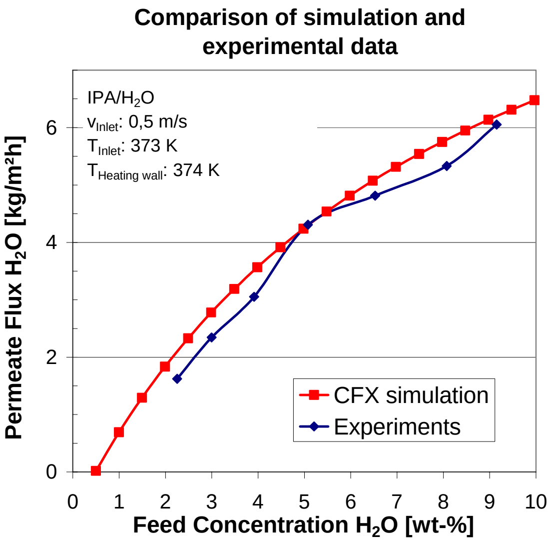


Figure 2.10 *Comparison of the simulated and experimental results of the Isopropanol dehydration by pervaporation at 100°C with silica membranes*

With the above described model for pervaporation, simulations of a typical industrial solvent dewatering application (IPA/H_2O) were executed. This combination of fluid dynamics and process design modelling should give a more accurate answer to the overall membrane area demand in a pervaporation process. In the stand-alone process design (e.g. with Aspen Plus) the permeation is extrapolated over the whole range of temperature and concentration on basis of experimental data, obtained on lab scale. This procedure already regards partly polarisation effects as they occur in the experiments, but does not take into account the effect of different hydrodynamic situations and their impact on the performance. Furthermore the increasing relevance of polarisation with increased permeation cannot be described. This is the major advantage of the combined model approach.

Especially the solvent dewatering case is technically characterised by combined big temperature (T) and concentration (w) drop along one module and subsequently along the series of modules in a complete pervaporation plant. Parameters, T and w, influence the separation efficiency significantly via feed properties and the overall level of water permeation. For the calculation a constant module size of 25 m² was assumed. All relevant process data of the pervaporation plant, like flow rate and temperature/concentration at the feed, were obtained from a previously executed process design. Contrary to the findings of the stand-alone process design (5 modules with total 125 m^2 of membrane area), 7 modules with a total membrane area of 175 m² are required to meet the product specification of 0.1 wt.% water (see Figure 2.11). This equals an increased membrane demand of 40 %, which would significantly influence the quantitative result of an economic evaluation.

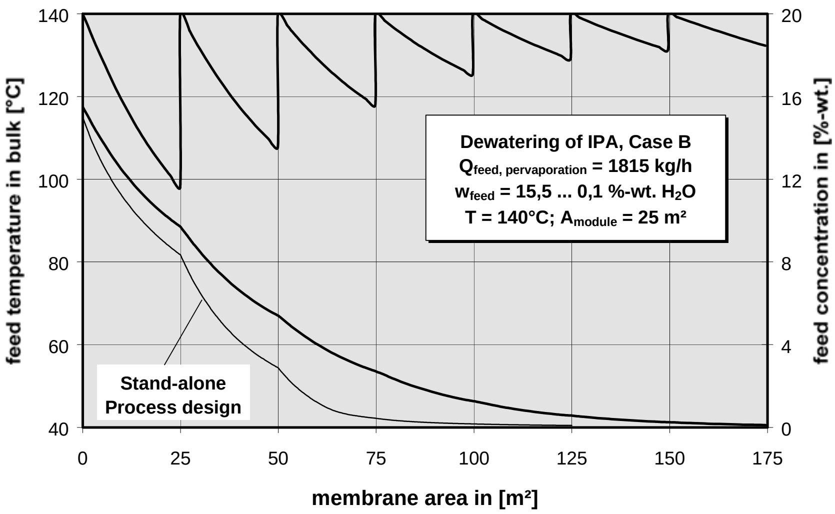


Figure 2.11 *Result of combined process design with fluid dynamics calculation, IPA-dewatering*

Calculation of heat transfer in the module with the developed model
The model is further capable to calculate the (iso)thermal operation of the SMS® module with steam heating or thermal liquids. For the choice of the heating medium, the operating temperature of the module in a certain application has been taken into account. The heat transfer is optimal at the feed inlet due to entrance effects. The feed temperature is not exactly uniform over the whole module. At the inlet where the feed concentration and thus permeate flux are high, strong cooling results in a somewhat lower operating temperature, while towards the outlet the feed temperature rises again because of the reduced flux.

To ensure a constant operating temperature of the isothermal module concept Pervap® SMS, (see Figure 2.6) sufficient heat can be provided by either steam condensation or a thermal liquid. The heat transfer has been calculated for both the heating cases and altogether, the heat transfer by steam condensation is 50 to 100 % better than when using a thermal liquid, see Figure 2.12.

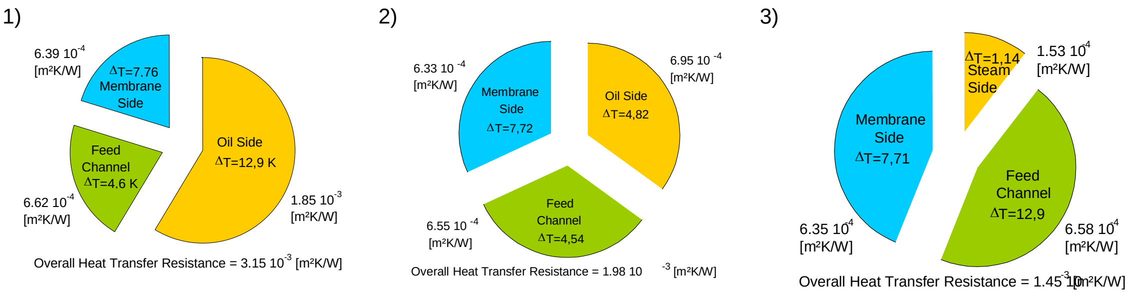


Figure 2.12 *Composition of the overall heat transfer coefficient from the resistances in the single boundary layers for different heating principles. (1) thermal liquid with 2 m^3/h, (2) thermal liquid with 10 m^3/h, (3) steam condensation*

The size of the annular duct in the SMS®-module has a major impact on pressure drop and heat transfer due to the velocity of the feed. The influence of the gap distance between the membrane tube and the heat exchanger steel tube on the heat transfer coefficient has been calculated indicating a better heat transfer with increasing gap size. In Figure 2.13 the correlation between Reynolds number, heat transfer coefficient and gap distance can be seen. Furthermore it has been found that counter-current heat supply leads to slightly better heat transfer than co-current flow.

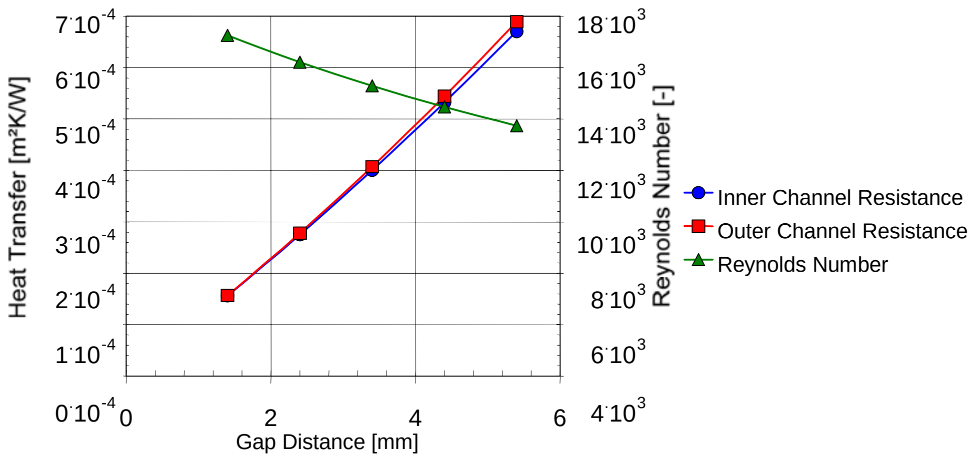


Figure 2.13 *Effect of the Annular Duct Size on the Heat Transfer*

Module arrangement

In general a larger scale pervaporation system contains several membrane modules. Depending on the arrangement of the modules the system can be optimised towards for example less membrane area or low pump energy use. In the EXCEL-programme, an arrangement of 6 modules has been implemented as part of an optimisation study for an imaginary (but realistic) process. Five arrangements have been modelled. The different arrangements (see Figure 2.14) have an important impact on the feed pressure drop and feed water depletion.

Six modules arranged in a row reach the best depletion of a 10 wt.% water/IPA mixture down to 2.1 wt.% because of the lower polarisation effects and higher heat transfer coefficient at the high feed velocity. The major disadvantage of this arrangement is that the high Reynolds number leads to a high-pressure drop. The so-called fir-tree structure (2 and 3) which is often used for desalination with reverse osmosis is not the best arrangement in terms of pressure drop and depletion since the permeate flux, compared to the RO, is much lower. Arrangement 5 with 2 x 3 modules in a row shows a slightly better performance. It builds the best compromise between pressure drop and the needed membrane area for the depletion. However, the pressure drop is not the only design parameter and concerning costs not the mayor one. Comparing the costs for pumps (including energy consumption) with the membrane costs a different point of view turns out. The membrane costs are exceeding the costs for pumps and energy. On one hand the high pressure drop of set-up 1 leads to a two pump system. On the other hand the high turbulences are reducing the needed membrane area for a depletion from 10 to 3 wt.% by about 15% compared to set-up 2, 3 and 5. This saving in membrane area justifies the higher pump and energy costs. The conclusion is that an even expensive effort for reducing membrane area pays off as long as the membrane price dominates the total price.

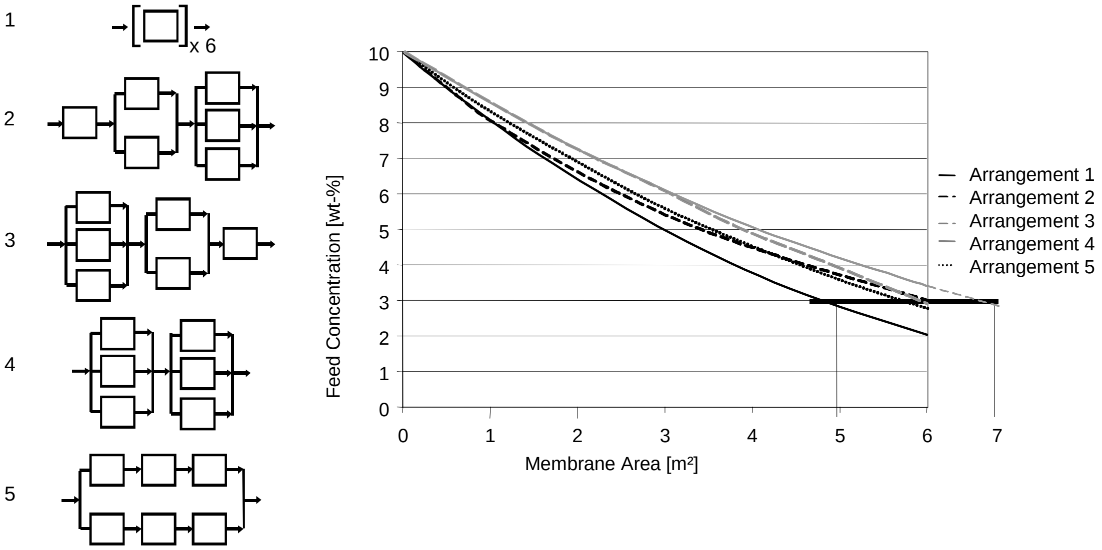


Figure 2.14 *Module arrangement with 6 modules*

Final design

The liquid flow through the annular gap between the tubes, the openings at the return manifold in the tube sheets, and the resulting pressure loss, mass and heat transfer have been modelled by Aachen. The calculated data have been compared to those measured in single tube and two tube modules at Sulzer. Measured values and calculated results were in good agreement. Optimisation by CFD calculations and in the design and manufacturing have led to an acceptable compromise, and the pressure losses on the feed side could be reduced to the same values as with modules in which only one membrane tube is housed in a heat exchanger tube. Especially for larger membrane area modules a new design offers a significant cost reduction.

Several full size industrial modules have been engineered and built, following both the concepts of single and two side permeate outlet. Module housings of 5 m^2 or any multitude of this figure are preferred, resulting in modules with 5, 10, and 20 m^2. For two of the latter sizes final drawings and design were finished, quotations collected, and the modules ordered from a manufacturer. The design of the module has followed the experience gained so far in the laboratory, and all improvements recommended by the different CFD calculations have been considered. A client has placed a first order for a solvent dehydration plant into which several 10 m² modules have been installed. The respective pervaporation plant shows a very simple design, as the feed side piping is reduced to a simple connection of the modules.

2.4 Work package 3 Testing

2.4.1 Aim

To test the performance (flux, selectivity, stability) of the membranes and systems in the selected applications on lab and pilot scale as a function of the composition and temperature of the feed mixture, and the influence of feed flow pattern and permeate side pressure and pressure loss. To support the design of the module and systems by this testing and to test the functionality of the modules on a semi-industrial scale. Main results: experimental results of the performance (flux, selectivity, stability, etc.) of the membranes systems on pilot scale, functional test of the semi-industrial scale module, and a validated computer programme for general engineering calculations of pervaporation and vapour permeation plants.

2.4.2 Pure components and binary mixtures

In Table 2.1 pure component and mixture permeances of different alcohols and water are compared on basis of the previously obtained permeation experiment data. Remarkable is the comparison of the pure water permeance to the one in the mixture. The drop by a factor of six is caused by concentration polarisation effects, which are a crucial issue in module design. Due to the vapour-liquid-equilibrium for methanol and ethanol, membrane selectivity is higher than the process selectivity, while for IPA and n-butanol it is vice versa.

Table 2.1 *Pure component, mixture permeances and ideal, process and membrane selectivities for alcohols and water*

Components	*Pure Permeance [kg/m²h]*	*Mixture Permeance [kg/m²h]*	*Ideal Water Selectivity [-]*	*Process Selectivity [-]*	*Membrane Selectivity [-]*
Water	75,46	11,52	-	-	-
Methanol	0,76	1,09	100	10	30
Ethanol	0,45	0,52	165	55	65
i-propanol	0,58	0,38	130	90	80
n-butanol	0,13	0,11	240	930	160

Binary mixture permeation experiments at about 10 wt.% water and 10 mbar permeate pressure and different feed temperatures were performed to investigate the use of silica membranes in dehydration applications. The membrane screening included a total number of 34 organic solvents from classes like alcohols, aldehydes, carboxylic acids, esters, ethers, ketones, amines, nitriles, phenols, and halogenated hydrocarbons. The diagram of a plot of the partial water flux over the partial pressure difference from feed to permeate in Figure 2.15 gives a rather good overview on the obtained results. Mixtures with ketones and ethers have the highest water fluxes, glycols the lowest at the same driving force. The performance of amines, nitriles, alcohols and carboxylic acids is in an intermediate region. The values for the permeance for different classes of systems are shown in Figure 2.16. The flux rates of 10 to 20 kg/m²h per bar partial pressure difference of water from feed to permeate represent a new dimension in solvent dehydration. The permeance for the solvents are very small except for the esters and carboxylic acids so that the membrane selectivity is excellent for the majority of the systems.

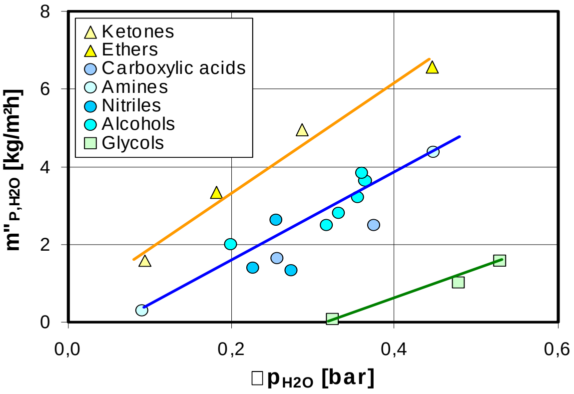


Figure 2.15 *Partial permeate flux of water over partial pressure difference*

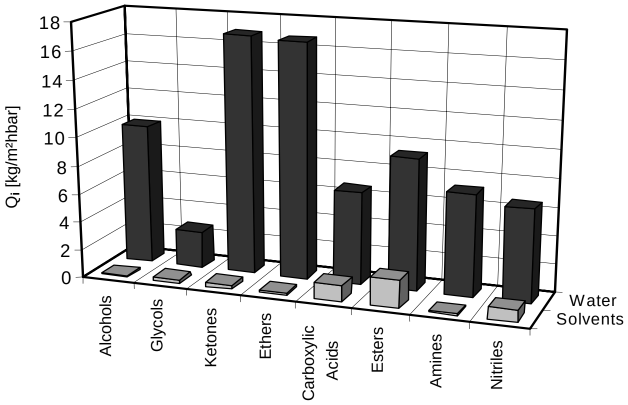


Figure 2.16 *Permeances of the silica membrane for solvent and water in different classes of systems*

The dewatering of THF has been been studied in more detail. In general very high fluxes and reasonable selectivity are obtained in THF dewatering. Furthermore it has been shown that dewatering of the azeotrope (7 wt.% water in THF) is possible. After 11 days of testing in THF a 10% water flux decline in the standard BuOH test was observed, without change of selectivity.

The initial aim of dewatering high boiling glycols was to analyse the behaviour and the removal of high boiling components at the backside of the membrane, below its boiling point at vacuum conditions. After starting up the water concentration drops from about 95 to 76 % within 2-3 hours reaching a minimum and rises again. This behaviour can be explained by the membrane support being soaked by the process liquid during the wetting period. Starting up the system the water evaporates first and is collected in the condenser. Subsequently more high boiling component evaporates and the permeate purity decreases and then slowly increases again up to the initial permeate purity when all high boiler is evaporated. A start up procedure was made to reduce this phenomenon as far as possible. On industrial scale this behaviour should be accounted for in the starting up of a plant.

For the performance tests of separating non-polar/water mixtures a system of toluene and water has been chosen. The permeate purity is falling from 35 wt.% water in the permeate at 0.7 wt.% in the feed down to 2 wt.% at 0.1 wt.% water in the feed as expected, as the driving force for water is decreasing. The corresponding permeate fluxes are showing a different behaviour. The flux varies between 4 and 6 kg/m²h scattering around, which can be explained by difficulties in taking samples. In contrast to polymeric membranes the inorganic membranes have shown to be able to dewater a feed with very low water concentrations.

2.4.3 Chemical stability testing

The chemical stability of the amorphous silica membrane in almost all solvent water mixtures was excellent except for some carboxylic acids, esters and alkaline amines. As the membranes will be used in the dewatering of acid or alkaline containing liquid mixtures they have been tested for their stability.

Alkaline stability tests have been performed with the system ethylene-diamine/water at a feed temperature of 100°C with an initial water concentration of 90 wt.% and a permeate pressure of 20 mbar. The pH of this feed mixture was about 10 to 11. After less than 20 minutes the membrane was attacked by the base that seriously that the flux increased so much that the permeate side of the experimental set-up was flooded with liquid and the vacuum broke down.

For acetic acid/water with a water concentration of 50 and 70 wt.% and at a feed temperature of 100°C and permeate pressure of 20 mbar, the membrane performance over operation time is shown in Figure 2.17. The permeate flux shows an increase from 11 to 15 kg/m^{2}h in the first three hours and oscillates around 13±2 kg/m^{2}h in the following 7 hours. The permeate concentration of water decreases steadily from 99 to 77 wt.%. Standard pervaporation tests with water-IPA showed that the silica membrane is damaged after about 12 hours in the acetic acid/water mixture. The pH of the feed liquid has not been measured.

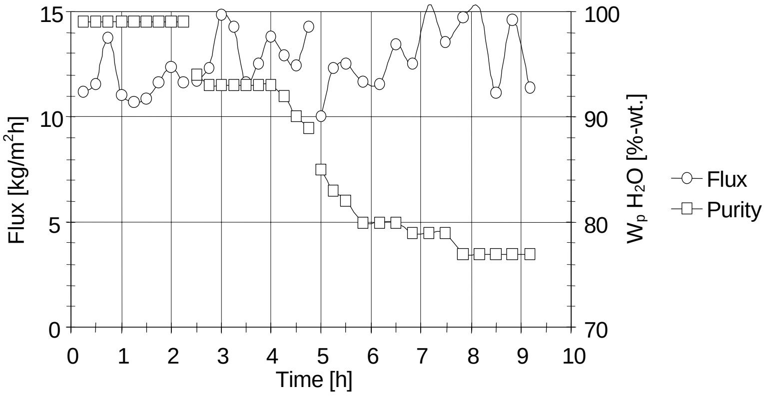


Figure 2.17 *Flux and permeate concentration of membrane S0-5-8/1 in acetic acid/water*

To test the effect of different pH levels on the membrane stability, a new experiment using several acetic acid - water mixtures have been used: pH = 0, 1, 3, and 5 and 5% HAc in 96% EtOH + 4% water. All experiments have been performed at 25°C. After 10 days at pH = 3 the membrane did not show any changes compared to a fresh prepared membrane. At pH = 1 the membrane was attacked after 10 days.

The membrane stability problems in acid and alkaline solutions have to do with both the silica membrane layer and especially with the underlying gamma-alumina layer. Outside the project a new membrane has been developed in which the silica layer was replaced by zirconia. Pervaporation fluxes are comparable with the silica membranes and the selectivity was only slightly lower: 5 wt.% water in n-BuOH at 75°C led to a permeate containing about 92% water and a total flux of 4900 g/m^{2}h was measured, see Figure 2.18. The membrane was tested in acetic acid-water mixtures at different pH values and in mixtures of 5 wt.% of HAc in ethanol or butanol, all at room temperature. No attack of the zirconia layer was observed even after 10 days at pH=1, see Figure 2.19.

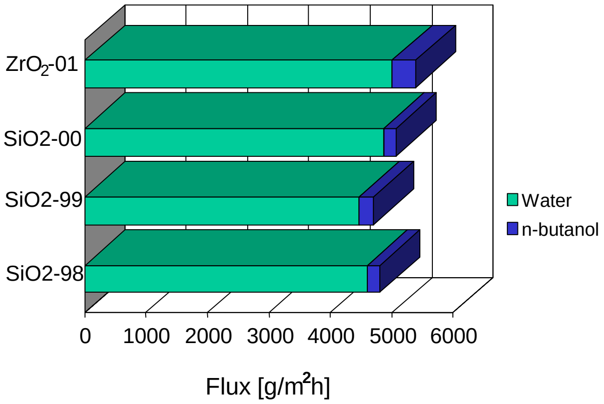


Figure 2.18 *Fluxes for silica and zirconia membranes in dewatering of BuOH*

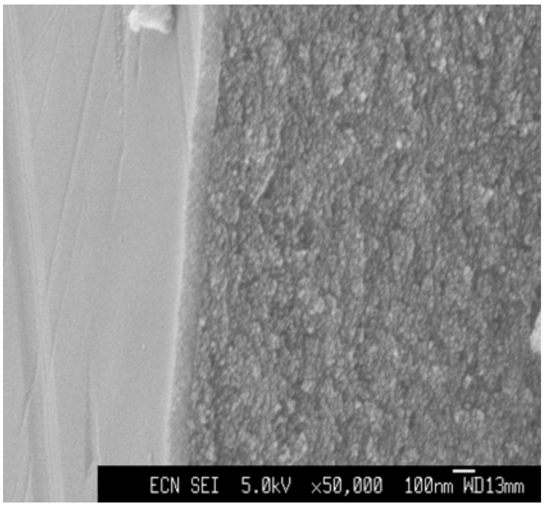


Figure 2.19 *SEM micrograph of zirconia membrane on gamma alumina after 10 days at pH = 1*

2.4.4 Lab scale testing for Lyondell's processes

The microporous silica membranes have been used for dehydration of several process mixtures of Lyondell. The mixtures that have been dehydrated are TBA, A-fuel and glycol. First tests on lab scale have been performed, which should give an indication of the membrane performance in general and the optimal process conditions for each pervaporation process. These results have been used as input for pilot scale testing at the location of Lyondell. The results of the lab scale tests are described in this section, in the next section the results of the pilot testing will be given. In the last section on Lyondell's processes testing some vapour permeation measurements are compared with the lab scale and pilot scale pervaporation results.

Lab scale TBA testing

The measurements have been performed with a TBA mixture of Lyondell, which contains initially about 0.6 wt.% water. The wish of Lyondell is to dewater the feed to a lower water content. Testing has been performed at three different temperatures: 75, 95 and 105°C. As expected, the flux increases with temperature and the permeate concentration decreases with a decrease of the feed water concentration. At very low feed water concentrations the permeate contains only a limited amount of water, but still more than 30 wt.%. This water increase still corresponds with a selectivity of 428.

After these measurements the dewatering of three batches of TBA at 95°C has been done using one membrane. The results of the batch dewatering measurements are presented in Figure 2.20. The behaviour is as expected. The water concentration decreases in time as more water permeates than TBA does. This decrease takes longer the more the feed water concentration has decreased, as the driving force for water transport decreases with the feed concentration. The flux was stable over all three batches measured. The water concentration in the permeate even increased somewhat from batch 1 to batch 3. The results have been used to calculated the dewatering with the pilot unit. If a membrane system with 1 m^2 membrane area is being used to dehydrate 250 l of TBA it will take about 5.5 hours. The permeate will then contain about 85 wt.% of water.

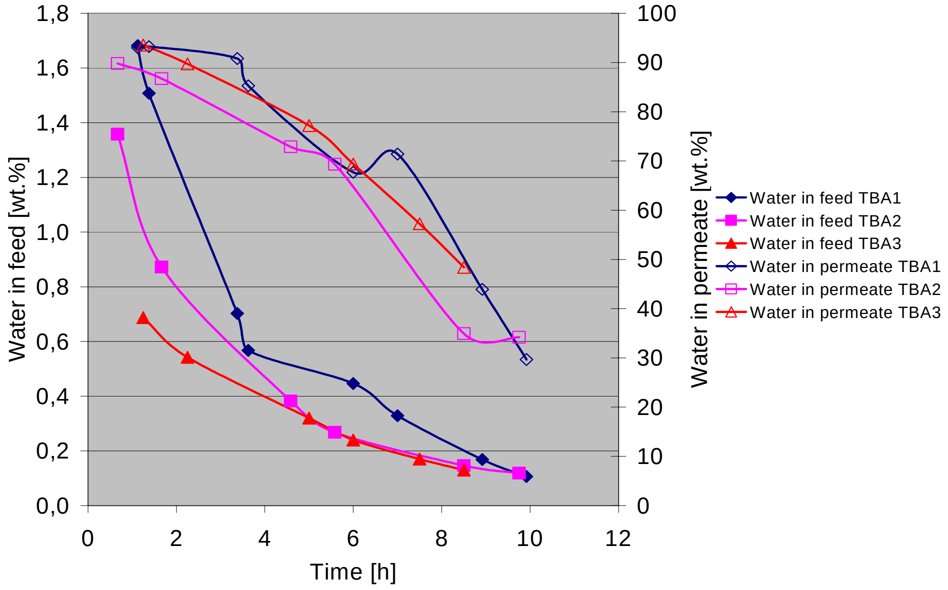


Figure 2.20 *Results of dewatering 3 batches TBA at 95°C*

Lab scale A-fuel testing

The main incentive for the batch dewatering of A-Fuel is to decrease the water concentration in the feed and thereby increase the caloric value of this mixture with alcohols, ketones and heavies. The measurements with the A-fuel mixture, which contains water, have been performed at three different temperatures: 50, 75 and 100°C. Again the flux increases with an increase in temperature. From 50 to 75°C and from 75 to 100°C the flux increases by respectively a factor of 4 and 3. The permeate concentration is high, even though the feed contains components like acetone, methanol and methyl-ethyl-ketone.

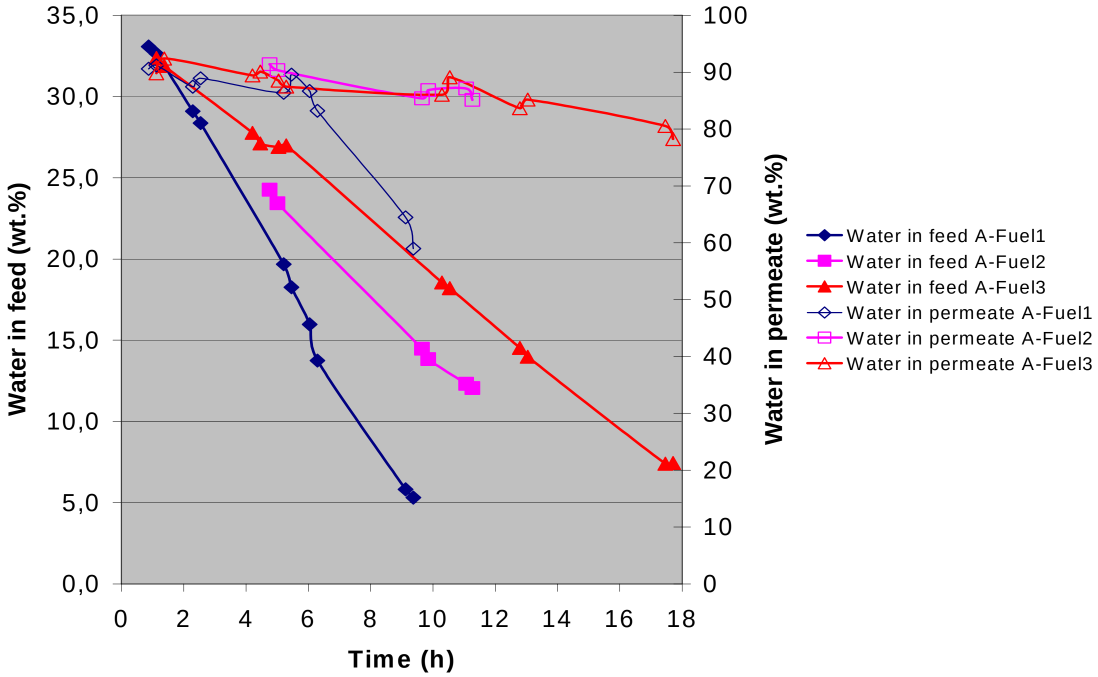


Figure 2.21 *Result of dewatering one of the three batches A-fuel at 75°C*

After these measurements the dewatering of three batches of A-fuel at 75°C has been done using one membrane. The results of these batch dewatering measurements are given in Figure 2.21. At feed concentrations below 10 wt.% water, the water flux decreases rather strong and the permeate purity drops below 80%, which is still very good. The rather strong water flux decrease maybe has to do with a strong decrease in driving force, but as the feed mixture is a multi component mixture, the driving force cannot be calculated. During the dewatering the membrane changed colour from white to yellow-braun due to some deposition on the membrane surface. This is most probably the reason for a flux decline of about 15% as measured by a pre- and post pervaporation test with a standard water-butanol mixture. The data are used for calculating the time needed for dewatering with the pilot unit. If a membrane system with 1 m^2 membrane area is being used to dehydrate 250 l of A-fuel it will take about 12.5 hours. The permeate will then contain about 85 wt.% of water.

Lab scale glycol testing

A process mixture of Lyondell consists of MPG, DPG and TPG (mono, di, tri propylene glycol) and water. In the process at Lyondell water is removed by distillation, however, for increasing the capacity pervaporation is an option. Initial tests using a process mixture of Lyondell have been done before any larger scale testing was started.

The water flux at 100^{o}C is about 3.5 kg/m^2h and is almost stable over the measurement period of 4 hours. The permeate contains about 99 wt.% of water. The influence of the temperature and permeate pressure on the flux is presented in Figure 2.22. As expected, the higher the permeate pressure, the lower the water flux as the driving force decreases. Again the water flux increases exponentially with temperature and the glycol flux increases from about 4 g/m^2h at 60°C to 48 g/m^2h at 120°C.

In a batch experiment the propylene glycol mixture has been dehydrated at 100^{o}C. The water concentration in the feed vs. time is presented in Figure 2.23. Overall the permeaat contained more than 99 wt.% water, the average water flux was 860 g/m^2h and the glycol flux was 5 g/m^2h.

By standard testing it was shown that initially the membrane is very good but during the several tests with the glycol mixtures a flux decline is observed. This flux decline could be caused by the blocking of pores as glycol has a high boiling point and is maybe not completely removed (evaporated) by the vacuum or could be due to the flux decline of the (pure) silica membrane as reported in WP4 of this technical section.

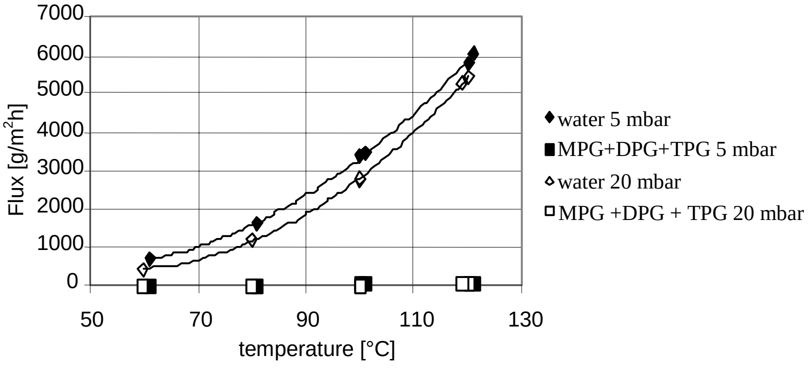


Figure 2.22 *Influence of temperature and permeate pressure in glycol mixture dewatering (feed 12.5 wt.% water)*

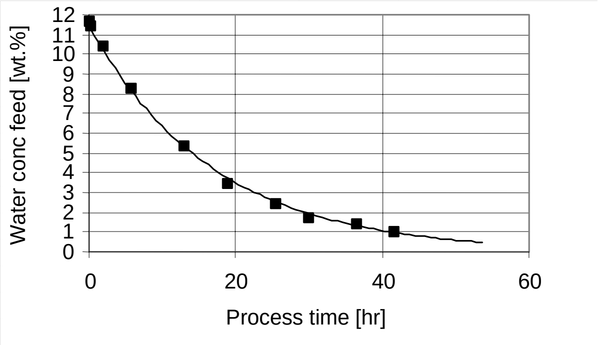


Figure 2.23 *Batch dewatering of glycol mixture at 100°C and 10 mbar*

2.4.5 Pilot scale testing at Lyondell

The microporous silica membranes have been used for dehydration of several process mixtures of Lyondell. The mixtures that have been dehydrated are A-fuel and glycol. TBA has no been tested on pilot scale as the permeate flow is very low because of the low feed water concentration, which would lead to measurements being inaccurate. The lab scale test results as described in the previous section have been used as input for pilot scale testing at the location of Lyondell using the test system as described in Figure 2.5 and a maximum feed amount of 1000 litre. The results of the pilot testing are described in this section.

A-fuel pilot scale testing

A testing program for A-Fuel of Lyondell has been set up and it was decided to test the influence of the feed flow and the temperature on the membrane performance and then perform a batch dewatering at a constant temperature of 95°C.

The results in the influence of feed flow and temperature meet the expectations; a higher feed flow gives a higher Reynolds number leading to less concentration polarization and thus a higher flux. A higher temperature also gives a higher flux. The water concentration in the permeate is 93 wt.% which is sufficiently high, and it is even higher than what has been measured on lab-scale.

As indicated in the lab scale dewatering of A-fuel, the main incentive for the batch dewatering of A-Fuel is to decrease the water concentration in the feed thereby increase the caloric value. This batch dewatering has been done at a temperature of 95°C using a membrane area of 0.323 m^2 and a feed amount of about 300 litres using the pilot scale installation as given in Figure 2.5. The experiments have taken several days and the results are shown in a summarised way in Figure 2.24. In this figure the feed water concentration and selectivity (during the batch dewatering of the A-Fuel) are shown as a function of the process time. Also the selectivity is fitted with a 3rd degree polynome.

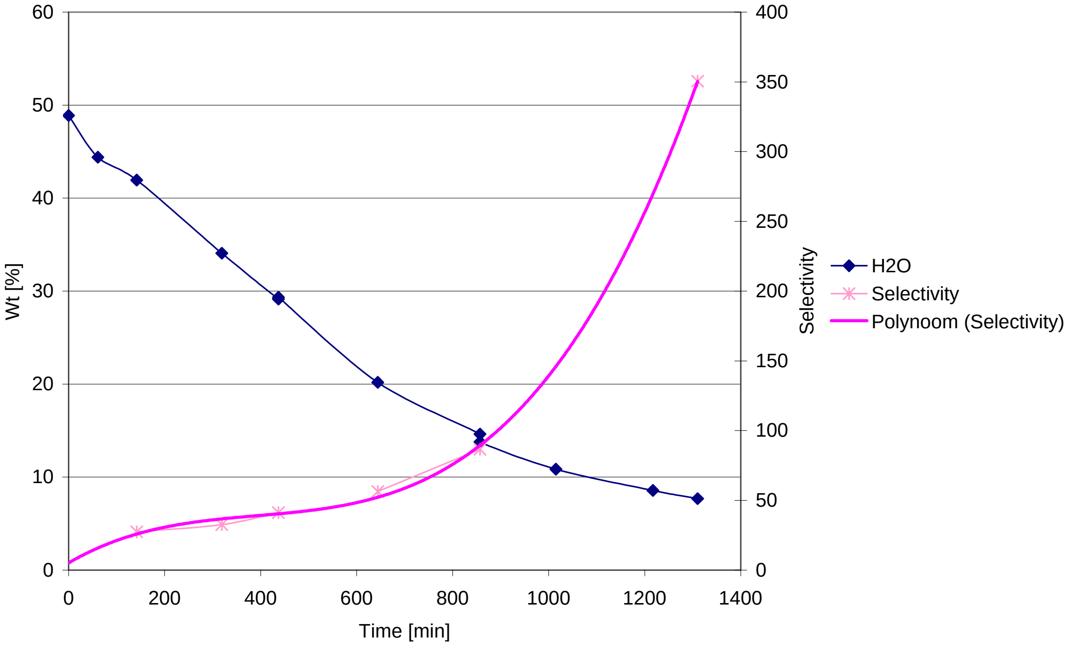


Figure 2.24 *Behaviour of the components of A-Fuel in the feed, T-95^{o}C*

The decrease of the water concentration is a straight line rather than a nice curve. This has been seen on lab-scale as well. It is possible that the driving force hardly changes during the dewatering. A large increase is seen in e.g. the IBOH, TBOH and heavies concentration in the feed. A smaller increase is observed for some of the other components, which is due to the fact that water is being extracted from the feed, so the concentration of the other components must increase (if they are not permeating).

Figure 2.25 Describes the permeate compositions in time. Amongst water, the main component that is permeating is MeOH (as expected). The selectivity increases in time is, when compared to e.g. distillation, very acceptable. The water concentration in the permeate stays very high, always above 93%. This is in contrast with the lab-scale experiments in which a decrease of water concentration in the permeate was seen in time, especially when the feed concentration dropped below 10 wt.% water.

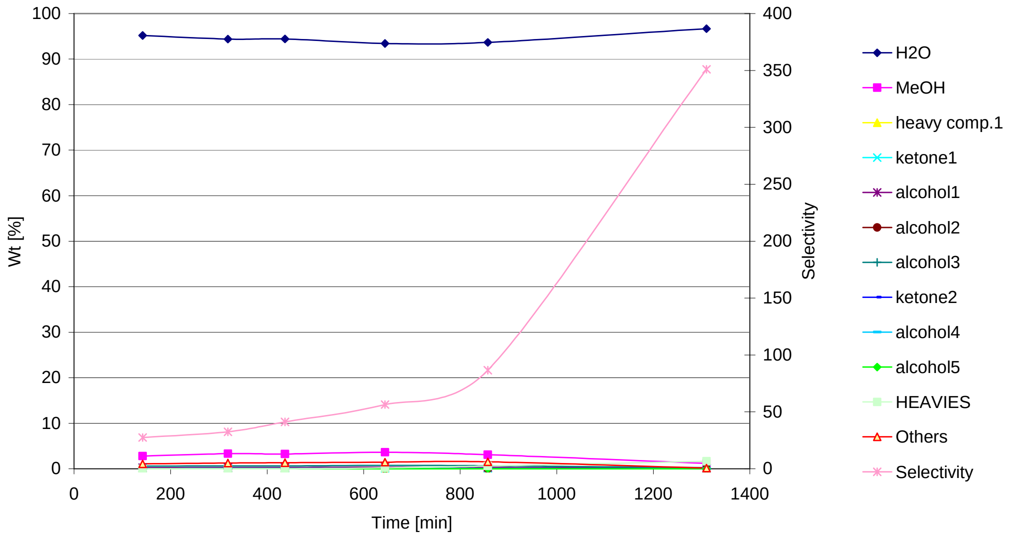


Figure 2.25 *Permeate compositions and selectivity in time*

The water flux in the experiments is decreasing in time, because of the decrease of the amount of water (= driving force) in the feed. However, the flux decline is stronger as expected from the water concentration decline only. When the membranes were dismounted from the module deposition on the membranes was clearly visible. The membranes were yellow/orange coloured and on some membranes a reddish deposition was visible. With SEM it was shown that there are depositions of iron (oxide) and calcium sulphate on the membrane. Most probably the fouling is coming from the tap water that has been used to clean the system. In lab scale testing demineralised water is being used and therefore no fouling was seen. The membrane fouling was also measured by a standard pervaporation test (95°C, 5% water in BuOH, permeate pressure of 10 mbar) indicating a water flux decline by a factor 5.

As the a decrease of water in A-Fuel should lead to a higher caloric value, the caloric values of the original A-Fuel and of the dewatered A-Fuel have been compared. See Table 2.2.

Table 2.2 *Results of caloric value measurements*

	Before dewatering	After dewatering
Caloric Value	21.215 MJ/kg	27.660 MJ/kg

An increase of 30% of the caloric value is achieved, by reducing the amount of water from 48% to 7%. A remark should be that the amount of acetone has also decreased in the dewatered A-Fuel (flashing by nitrogen bleed gas in the feed vessel). With acetone, the caloric value would even have even been higher. An increase in caloric value means that less A-Fuel is needed to provide the same amount of energy. However, the total amount is less but the selling price can be higher. All these results have been used for the economic evaluation in work package 1.

Glycol pilot scale testing

Crude MPG is a mixture of water in mono-di and tri propylene glycol. The aim of Lyondell is to reduce the amount of water in the feed. A total of 10 membranes with a membrane surface area of 0.404 m^2 has been used. The feed vessel was filled with 350L of crude MPG. A testing programme has been set up in which first the influence of temperature has been examined and then a batch has been dehydrated at 95°C.

The fluxes are similar to what was measured on lab scale. The flux at 75°C is a bit low compared with the other two measurements. The water concentration in the permeate is much lower than expected.

In the batch dewatering experiment, only the water concentration in the samples has been analysed. The permeate concentration is much lower than expected, about 80 wt.% water (lab scale > 98%). Furthermore a small but steady flux decrease occurs. This may be because of contamination by some A-fuel present or blocking of pores by condensed glycol that does not evaporate at the feed temperature and permeate vacuum used or by the flux decline as discussed further on in WP4. Post test analysis of the membranes has been done indicating defects, which are visible, by microscopy and pervaporation tests showed low selectivity. The testing with Crude MPG did not lead to as good results, as measured on lab scale.

2.4.6 A-fuel dewatering by pervaporation and vapour permeation on lab and pilot scale

Besides pervaporation (PV), lab scale experiments with vapour permeation (VP) for dehydrating A-Fuel have been performed. The measured performance is summarised and compared with the measured performance of the lab and pilot scale pervaporation experiments in Figure 2.26.

Regarding the fluxes of the vapour permeation, the performance is comparable to the pilot scale experiments at Lyondell and the lab scale experiments at ECN. Reaching lower feed water concentrations of about 10 wt.% the VP water flux decreases almost to zero very quickly. The obtained water flux from the PV lab scale between 40-10 wt.% water in the feed is constantly 7 kg/m²h higher than the flux from the pilot scale PV process and VP. Regarding the permeate concentration and the selectivity a different behaviour for vapour permeation and pervaporation can be observed. The selectivities obtained from the ECN lab scale batch dewatering do not much differ from the VP results in the higher feed water concentration. When the feed water concentration decreases, the selectivities from lab and pilot scale pervaporation increase whereas for the VP it drops fairly linear.

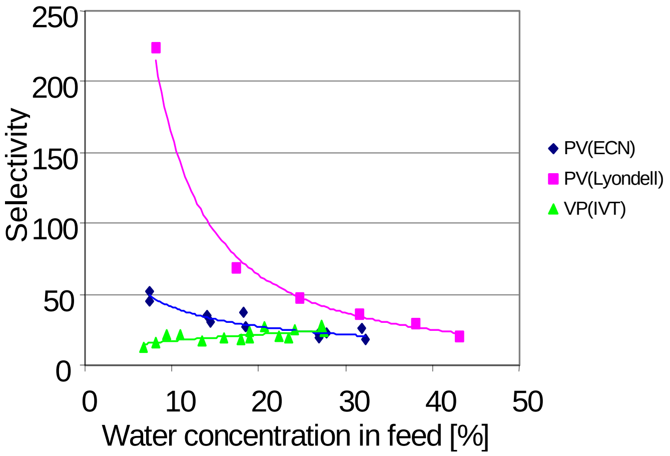


Figure 2.26 *Comparison of selectivity vs. water concentration in feed at 90°C*

Similar to pervaporation experiments the same reddish discoloration of the feed/retentate can be observed after the vapour permeation experiments. The colouring also appeared when no membrane was on stream. In contrast to the PV experiments, the colouring did not foul the membrane surface.

In general in vapour permeation fluxes and selectivities are comparable with pervaporation in the higher driving force region and lower at low feed water concentrations. Fouling seems to be less of a problem.

2.5 Work package 4 Membrane development and manufacturing

2.5.1 Aim

To make tubular silica membranes for the pilot module based on laboratory-made supports. To develop low-cost, robust pervaporation membrane tubes based on as commodity available support tubes. Establish a procedure for large-scale production of tubular ceramic membranes, based on low cost commodity supports. Main results: price efficient and robust inorganic pervaporation membranes and versatile coating techniques for different kinds of substrates.

2.5.2 Standard silica membrane development

The methods and techniques used to prepare the inorganic pervaporation membranes are described here. The support system for the silica membrane consists of 4 layers. The α-alumina macroporous substrate tube is made by ceramic paste extrusion followed by a sintering procedure. The standard diameter of the support tube is ID/OD = 8/14 mm. Tubes can be manufactured in a length up to 1 m. Before the final membrane layers can be applied two intermediate layers are applied to the support. The intermediate layers are coated on the support tube by a filmcoating technique using an α-alumina colloidal suspension. After drying a sintering step is involved ensuring consolidation. The so-called 'gamma' layer is applied onto the second intermediate layer by slipcoating of a boehmite sol. After drying and during a heat treatment this boehmite will transform to gamma-alumina. The silica membrane, which is the final separation layer, is made by means of sol-gel processing. Silicon alkoxide is hydrolysed by which a polymeric inorganic silica sol is obtained. This sol is coated onto the support followed by drying and calcination. All layers are applied on the outside of the tube. The structure of the different membrane layers can be seen in Figure 2.27. The thickness of the silica membrane as measured with SEM is in the range 100-150 nm. From gas permeance measurements the pore size has been estimated to be about 0.4 nm. The silica membrane layer is currently calcined at 400°C, which limits the operating temperature to 350°C. Because of the very hydrophilic nature of the silica and the small pores this membrane can be used for dehydration by pervaporation.

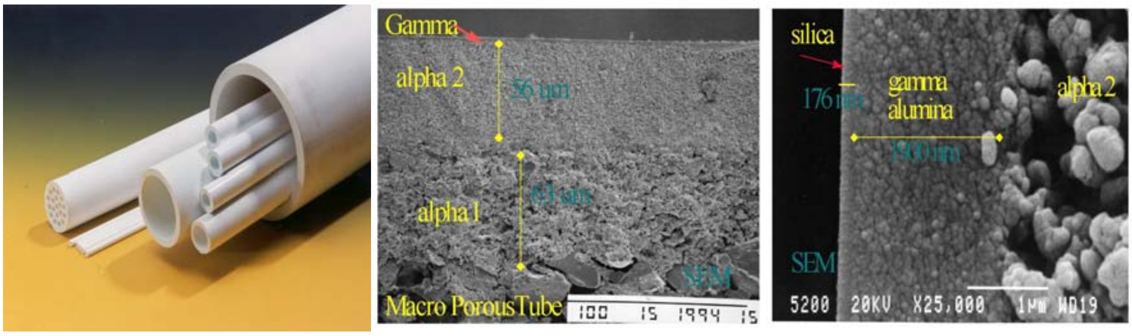


Figure 2.27 *SEM micrographs of silica membranes and membrane layers*

2.5.3 Commodity support choice and membrane development

To reduce costs for the final membrane production the membranes will be made based upon commercially available substrate tubes. The market for commodity, commercially available, ceramic membrane supports (tubular, single hole) has been screened. Samples of commodity supports have been received from Fairey (UK), Atech (Ger), Schumacher (Ger), TAMI (France/Germany) and ECO Ceramics (Nl). SCT (France) and HITK (Ger) have been contacted for receiving their supports as well. Characterisation of the supports has been performed. The supports have been coated on the outside with membrane layers and have been compared with the 'ECN-made' tubes. Based upon this discussions and negotiations with the potential suppliers were restarted in order to secure a steady, optimal and economical supply of porous ceramic tubes. Finally TAMI has made the best offer of material that meets the specifications and demands for large-scale production. A first batch of 3.000 tubes was ordered from TAMI and used for the development and production. These tubes have an inner diameter of 10 mm, an outer diameter of 14 mm, and are manufactured from aluminium oxide. Due to the requirements of the machinery for further coating of the base tubes very strict limitations for straightness, roundness, and inner and outer diameter had to be guaranteed by the manufacturer.

The TAMI supports have been characterised and coated with membrane layers both at lab scale at ECN and by Sulzer using a robot. Coatings of intermediate layers have been applied and characterised. The sintering procedures were optimised with the emphasis on translation and modifying of the lab scale recipes of ECN to the commercial scale of Sulzer and to be able to apply the different intermediate and membrane layers on the new TAMI substrates. The quality of the optimised final silica layer has been tested by helium flow and pervaporation tests. The different tubes have been compared with the 'ECN-made' tubes and showed good performance. A final translation of the ECN recipes to the robotised technique (see further) of Sulzer was then made.

The membranes, based upon TAMI supports, as made by Sulzer have been checked using a standard pervaporation test. The standard check is the so-called standard BuOH test, which is 5 wt.% water in n-BuOH at 95^{o}C and a permeate pressure of 10 mbar. A typical pervaporation result of the membranes as coated by the robotised system is given in the next table. Even though the membranes meet the targets, further improvements are being implemented as the membranes made on lab scale by ECN have a water flux, which is a factor 1.5 higher, and a butanol flux, which is a factor 3-4 lower than made by the robot.

Table 2.3 *Results of silica membranes on TAMI supports made by the robotised technique*

Membrane	*1*		*2*	
Measurement	1	duplo	1	duplo
Water flux (g/m2.h)	4193	4410	4689	4473
Butanol flux (g/m2.h)	343	342	279	237
Total flux (g/m2.h)	4536	4753	4968	4710
Water % in permeate	92,93	92,91	94,06	94,23

2.5.4 Silica membrane stability improvement

In dewatering of organic solvents an unexpected water flux decline in time was observed for the silica membranes, see Figure 2.29. From stability measurements on the different layers and pre-treatments of the standard silica membrane system it seems that water is causing the problem and that something is happening to the silica layer and not to the gamma-alumina layer and that adsorption only plays a role during the first few days of measuring. In order to solve the flux decline problem, membrane specifications were set to a certain minimum water flux for 5 wt.% water in BuOH at 95^{o}C, a maximum flux decline of 10% per year, and > 92 wt.% water in the permeate.

It is known that the silica membrane contains species, especially 3-rings of Si-O-Si and strained Si-O-Si bonds that are not very stable. These rings could open and/or the bonds could break and thereby decrease the pore size and thus the (water) flux. Stability improvement focused towards changing and/or slowing down the reactivity of the silica species. Far the best improvement in flux stability is obtained by incorporating methyl groups in the silica sol. These methyl groups are expected to positively influence both the adsorption and the stability of the silica structure. This addition of methyl groups in the silica structure has been done by the addition of and reaction with methyltriethoxysilane (MTES), see Figure 2.28 in the silica sol. This had led to the first generation of the so-called methylated silica (MeSi) membrane. Further optimisation has been done by using different concentrations, reflux times, additions speeds, addition sequences, coating concentrations, amount of coatings, and sintering conditions like temperature and conditions (air or nitrogen). This finally has led to a (second generation) MeSi membrane, which has a higher selectivity than the first generation MeSi membrane.

In Figure 2.29 pervaporation results for a silica membrane and a first generation methylated silica (MeSi) membrane are presented as a function of time. It can be seen that the methylated silica membrane is more stable than a standard silica membrane. The measurements have been performed at 75°C for a feed mixture containing 5 wt.% water in n-butanol. The MeSi membrane has a very good dewatering quality. There is still a slow flux decrease combined with a selectivity increase in time due to the faster decrease of the butanol flux than the water flux in time.

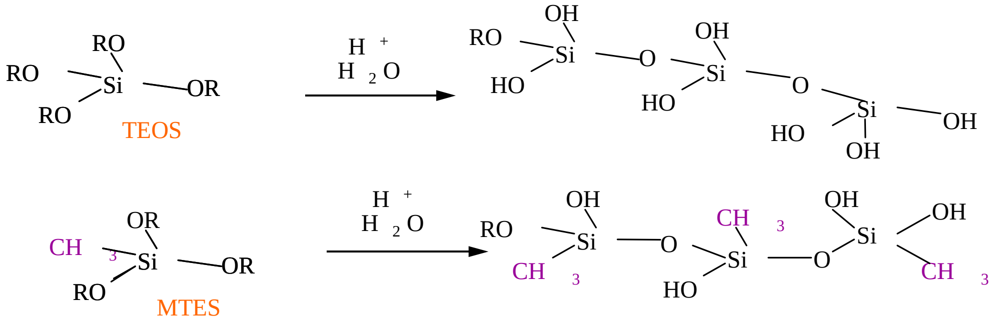


Figure 2.28 *Simplified reaction scheme for silica and methylated silica (MeSi) membranes*

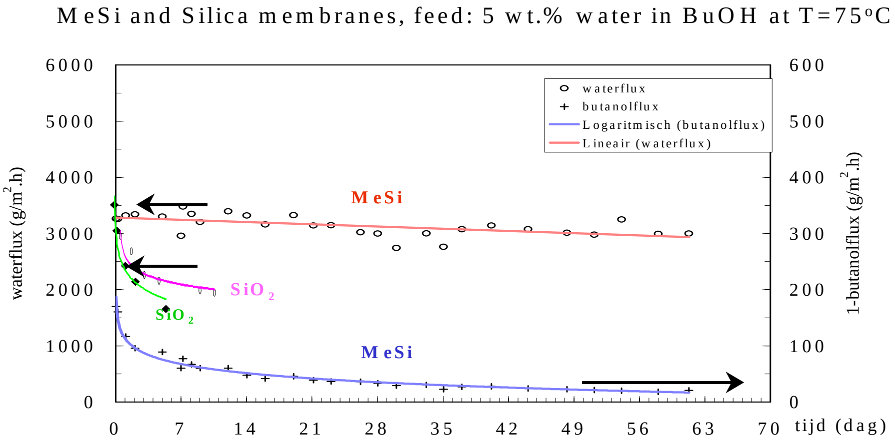


Figure 2.29 *Flux decline in time in days for silica and first generation MeSi membranes, feed = 5 wt.% water in BuOH at 75°C*

In Figure 2.30 the long term performance of a second generation MeSi membrane at 95°C is given. The membrane shows initially a flux decline of about 20% in 10 days but after this decline the MeSi membrane is almost stable at 95°C and it almost meets the specifications as set.

Several of the second generation MeSi membranes have been tested in pervaporation using 2.5 wt.% water in butanol at temperatures of 115, 135 and 165°C. The results are presented in Figure 2.31. After an initial slow flux decline in time the butanol flux suddenly increases after 20-40 days on stream. Also the water flux starts to increase. The membrane looses its selectivity. The higher the temperature the faster this process seems to be, though this conclusion is not yet very strong as only one membrane has been tested at each temperature. Pure silica membranes already show this selectivity decline after 4-7 days at 135°C.

The flux decline in the beginning of the measurements seems to be because of physisorption and can be reduced strongly by incorporation of methyl groups in the silica structure, as shown. After this first decline a metastable flux region is found, which is common to all silica membranes that have been studied. In this region a small (about 10-15% per year) flux decline is observed. In this regime a structural reorganisation of the Si-O-Si bonds occurs. The higher the temperature the faster this process and finally micro-cracks and defects are formed. The steric hindrance of methyl groups partly limits the structural reorganisation, but in the end also these membranes show selectivity loss. The use of thermodynamically more stable oxides can be considered as candidates for membranes stable at higher temperatures.

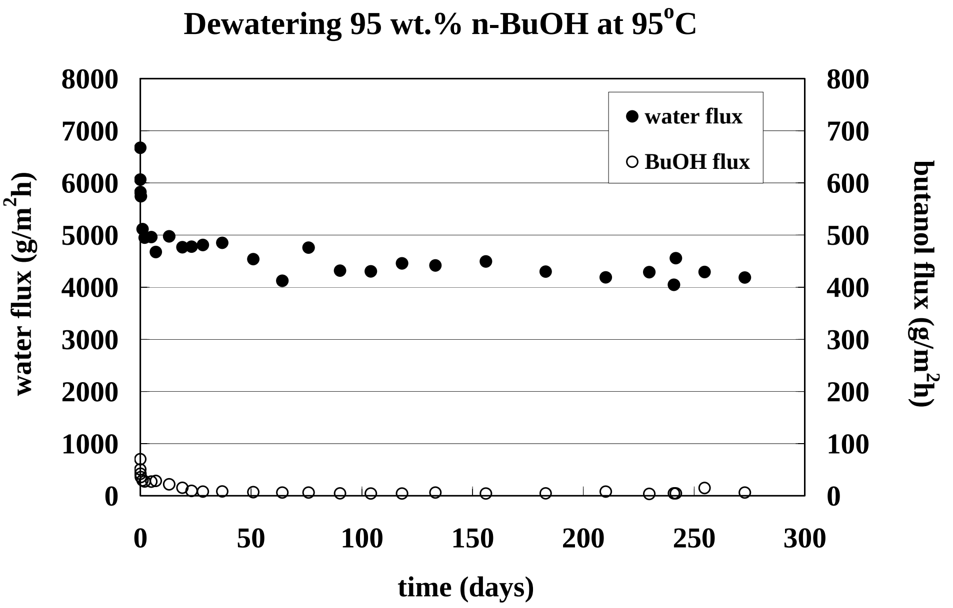


Figure 2.30 *Dewatering of 1-2 wt.% water in n-BuOH at 95℃, measured at 5 wt.% water in feed for second generation MeSi membrane*

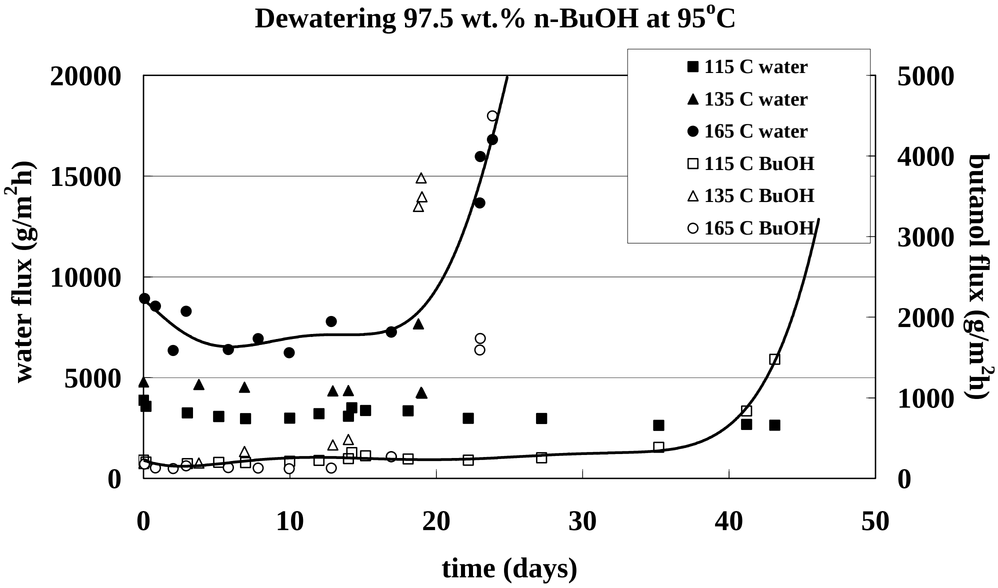


Figure 2.31 *Long term dewatering of second generation MeSi membrane at 115, 135 and 165°C, tested and measured at 2.5 wt.% water in the feed*

At the end of the project and for the moment for operation of these membranes in industrial applications, process conditions will be limited to a maximum temperature not exceeding 95°C. Up to this temperature the membranes have been tested more than 1 year in continuous operations, they perform well and meet the flux, selectivity and stability criteria set. From the stability tests it was clear that testing for only a few days does not give reliable information on the performance over a period of more than e.g. 100 days.

2.5.5 Setting up of membrane production facility

The lab scale membrane production procedures have been scaled up to a commercial production unit. For this a fully automated system for the coating of porous ceramic tubes was installed in a clean room of class 10,000 in order to avoid contamination of the final thin amorphous silica layer. The system is self-controlling and is designed to operate without human assistance. A robot picks up one tube, standing on a palette, at a time and passes it through the different treatment steps, dipping, drying, coating, see Figure 2.32. After passing through the respective steps of a coating cycle the coated tubes are placed by the robot onto ceramic palettes for sintering in one of the two kilns, each having a capacity of 200 tubes at a time. After the last calcination step a second robot will further process the membrane tubes. The length of each tube is measured; when necessary the coated membrane tube is cut to the specified length. One side of the membrane tube will be closed by a metal cap, to the other end a metallic interconnector will be fitted, which will seal the permeate side of the membrane to the feed side. Graphite rings effect the sealing between the ceramic tube and the metallic connectors. All these manipulations are performed automatically by the second robot. Both automatic systems have been installed. The production capacity of the membrane manufacturing system is designed for an output of 12,000 membrane tubes annually.

The production equipment has shown to work well, though debugging of especially communication between the two robots is still necessary. A first order for a pervaporation plant incorporating the ceramic membranes has been obtained from a client who is aware of the risk of a new technology. The membranes will be installed in SMS® -modules, a single tube in each heat exchanger tube. The feed in the annular gap between ceramic membrane tube and outer heat exchanger tube will be heated by steam; thus operation at nearly constant temperature will be secured. Larger scale production has started. For the final full capacity 1200 membrane tubes will have to be installed, with a total membrane area of 40 m². At the end of the reporting period more than 300 tubes have been manufactured and will be installed in a first module. After start-up the plant will operate with the first module at a temperature of 95°C with different solvents in order to gain experience in the operation and performance of membrane and modules under real industrial conditions. When positive results are obtained the residual membrane area will be produced and installed.

Figure 2.32 *Coating robot in clean room and coating stations*

3. LIST OF DELIVERABLES

Table 3.1 *List of deliverable items*

No.	Task	Timing (month)	Type *)	Description	Progress
D1	5	2	Re	Start-up document	Finished, sent to the EC in month 16
D2	1	3	Re	Choice of processes, set of specifications and starting points for developing test unit	Finished, sent to EC month 23
D3	4	6	Ha	Silica membranes for two 1 m^2 modules	Finished: available in month 6
D4	2	9	Ha	Two 1m^2 PV test units	All available in month 8
D5	1	12	Re	Choice of process configuration for 2 processes	Finished and sent to EC in month 34, including later changes with processes of Lyondell
D6a	3	18	Re	Test results basic testing and first 1 m^2 testing	Work finished, report combined with D6b
D6b	3	34	Re	Test results 1 m^2 testing	Work finished, report combined with D6a, and sent to EC in month 46
D7	4	24	Ha	Membranes for semi-industrial module	Finished: 24 membranes available for testing in month 24
D8	2	34	Ha	One semi-industrial module (about 5 m^2)	Module finished and incorporated in pervaporation plant in Italy
D9	3	41	Re	Test results of semi-industrial module	Work as integral part in plant delivery of D8
D10	4	41	Ha	Optimised membrane supports	TAMI supports available and membranes coated: good quality
D11	5	42	Re	Technology Implementation Plan	Finished and sent to EC in month 49 together with final report and costs

*) Re = Report, Ha = Hardware, So = Software

This PERSEP project is a follow-up of a pervaporation project that has run in the FP4 programme. For the previous project a summary open to the public has been written, which will be published in the FP4 programme overview. One of the main responses of the FP4 evaluator was that the energy savings as calculated for the pervaporation project was more that the sum of all 19 other projects that have been evaluated and significantly contributes to the EU policy.

1. Veen van, H.M., Replacement of energy consuming distillation towers by membranes, Project summary written for the FP4 impact assessment, May 2002.

Oral presentations and posters dealing with ceramic membrane preparation, the use of these membranes in pervaporation, module design, and possible energy savings by inorganic membrane pervaporation have been presented on several conferences. Furthermore some articles in papers have been written:

2. H.E.A. Brüschke, F. Marggraff, 'Isothermal module for high temperature pervaporation', abstracts of the lectures groups Thermal and Mechanical Process Engineering, International meeting on chemical engineering, environmental protection and biotechnology, Achema 2000, Frankfurt, May 22-27, 2000. Oral presentation.
3. H.E.A. Brüschke, P.P.A.C. Pex and H.M. van Veen, 'Isothermal module for high temperature pervaporation', abstracts 6th International Conference on Inorganic Membranes, Montpellier, June 26-30, 2000. Oral presentation.
4. N. Wynn, Pervaporation mit Keramikmembranen, CAV, Vol. 8, 2000, p. 72-73.
5. N. Wynn, Dehydration with silica pervaporation membranes, Membrane Technology, No. 129, 2000, p. 10- 11.

6. H.E.A. Brüschke and P.P.A.C. Pex, 'Isothermes Module mit keramischen Membranen für die Pervaporation', 8. Aachener Membran Kolloquium, 27-29 March 2001, Aachen, Germany, preprints,
7. S. Sommer, B. Klinkhammer, and T. Melin, Aspects of system design for dewatering of solvents with amorphous silica membranes, poster presentation at the 8. Aachener Membran Kolloquium, Aachen, Germany, 27-29 March 2001, preprints, page II-133.
8. S. Sommer and T. Melin, Design and optimisation of hybrid separation processes for dewatering of industrial solvents, poster presentation at the conference Engineering with membranes, Granada, 3-6 June 2001, proceedings Vol. I, page 369-374.
9. S. Sommer, Trennleistung anorganischer Membranen in der Pervaporation und Dampfpermeation - Aspekte der Verfahrensintegration, Oral presentation in German at the Arbeitskreis Keramische Membranen, 11. Oktober 2001, Bayreuth, Germany.
10. S. Sommer, Charakterisierung molekular trennender Membranen mit Permeations-experimenten, Oral presentation in German at the Arbeitskreis Keramische Membranen, 8. Mai 2001, Frankfurt, Germany.
11. S. Sommer, Th. Melin, Aspects of System Design for Dewatering of Solvents with Microporous Membranes, poster presentation at the International Workshop on Zeolite and Microporous Membranes, 1.-4. July 2001, Purmerend, The Netherlands, book of abstracts p. 83.
12. S. Sommer, Th. Melin, B. Klinkhammer, Inorganic Membrane Module Design: Modelling of Fluid Dynamics, IVT-Information, 31 (2001), 2, 3-14.
13. S. Sommer, Hybrid Separation Processes for Dewatering of Solvents with Inorganic Membranes, IVT-Information, 31 (2001), 2, 15-24.
14. H.M. van Veen, Y.C. van Delft, W. Bakker, C. Chau, S. Sommer and P.P.A.C. Pex, Energy savings by pervaporation with silica membranes, poster presented at the 7th International Conference on Inorganic Membranes (ICIM7) and the 5th International Conference on Catalysis in Membrane Reactors (ICCMR5), Dalian, China, 23-28 June, 2002 and the International Congress on Membranes and Membrane Processes (ICOM), Toulouse, France 8-12 July.
15. L.A. Correia and B.C. Bonekamp, Sol-gel silica membranes for energy efficient molecular separations, presentation at the Deutsche Keramische Gesellschaft - Nederlandse Keramische Vereniging Annual meeting, Eindhoven, 21-23 October 2002.

16. M. Schleger, Pervaporation und Dampfpermeation zur Lösungsmittelentwässerung mit mikroporösen Silikamembranen, 2002 Informationstag 'Stand der Membrantechnik im industriellen Einsatz' 2002 DECHEMA.
17. M. Schleger, S. Sommer and T. Melin, Solvent dehydration with Silica Membranes, Preprints Aachener Membran Kolloquium, P 4.14, Aachen, 2003
18. M. Schleger, 'Pervaporation and gas separation with ceramic membranes, presentation at the Deutsche Keramische Gesellschaft - Nederlandse Keramische Vereniging Annual meeting, Eindhoven, 21-23 October 2002.'

One PhD thesis has appeared. A second one will be finished in 2005.

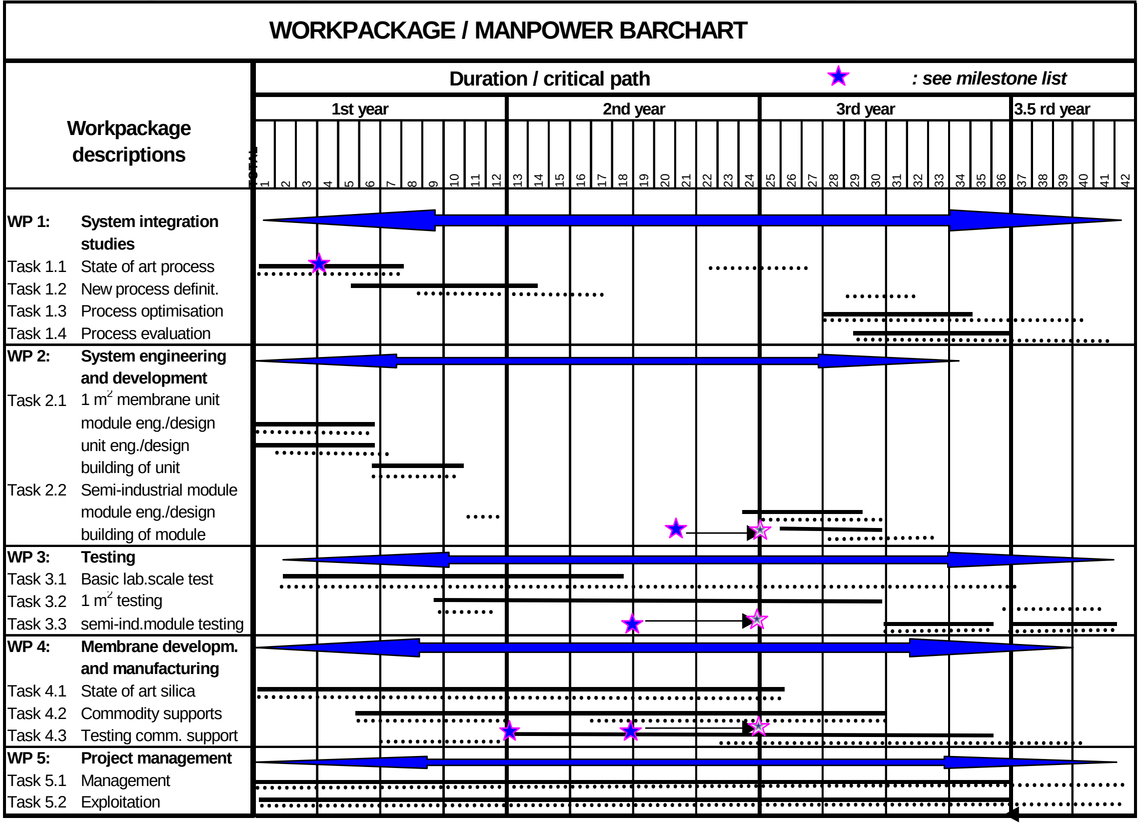
19. S. Sommer, Pervaporation and vapor permeation with microporous inorganic membranes, thesis RWTH Aachen, 2003, Verlag Mainz, ISBN 3-86130-084-2.

Exploitation

Sulzer Chemtech as membrane producer and pervaporation and vapour permeation system engineer has to evaluate and arouse the interest of potential users of the new technology. Information is disseminated via technical publications and direct contact to the respective industry, and by supplying membrane samples for laboratory tests to a selected number of end users. An order for a pervaporation installation based upon ceramic membranes has been received and the installation will be delivered summer 2003. It is anticipated that the production facility for the membranes will be in full operation end of 2003.

4. COMPARISON OF INITIALLY PLANNED ACTIVITIES AND WORK ACTUALLY ACCOMPLISHED

Table 4.1 *Updated work plan (original time schedule: black lines, the updated: dashed line)*



4.1 Comparison of planned activities and actual work accomplished (based on new work plan)

Most of the work was performed in conformity with the work programme. Delivery of the final reporting and the technology implementation plan was, however, behind schedule. In Table 1.1 the progress per task is given. In the last two columns the percentage completed vs. planned are given.

Table 4.2 *Progress per task*

Task	Description	Progress	% Completed (vs. planned) **New contract**
1	*System integration studies*		*100 (100)*
1.1	State of the art processes	Processes chosen, overview finished and reported in deliverable No. 2	100 (100)
1.2	New process definition	Extended with Lyondell processes, and reported in del.5	100 (100)
1.3	Process optimisation	Calculations finished for Lyondell processes	100 (100)
1.4	Process evaluation	Calculations finished for Lyondell processes	100 (100)
2	*System eng. and developm.*		*100 (100)*
2.1a	1 m^2 module engineering + design	Pilot (1 and 2 tube modules) and 1 m^2 module engineered and designed	100 (100)
2.1b	1 m^2 unit engineering and design	1 and 2 tube and 1 m^2 unit engineered and designed	100 (100)
2.1c	Build unit and module	Finished for 1 and 2 tube module and 1 m^2 system	100 (100)
2.2a	Semi-industrial module engineering and design	Module engineering finished as part of Italy plant	100 (100)
2.2b	Semi-industrial unit eng. and design	Finished for 40 m^2 unit	100 (100)
2.2c	Build unit and module	Finalised in May 2003 in Italian plant	100 (100)
3	*Testing*		*100 (100)*
3.1	Basic lab scale testing	Finished for several binary mixtures, stability testing is finished but also continued after the end of project, tests for Lyondell finished	100 (100)
3.2	1 m^2 testing	Finished for glycol and A-fuel at Lyondell	100 (100)
3.3	Semi-industrial module testing	Finished and partly combined with testing at Lyondell	100 (100)
4	*Membrane develop. + manufact.*		*100 (100)*
4.1	State of the art silica	Membranes available upon request. Stability guaranteed up to 95°C, for higher temperatures improvement needed	100 (100)
4.2	Commodity supports	Supports chosen and coated by ECN and Sulzer. Membrane production started.	100 (100)
4.3	Test commodity supports	Finished: good quality in pervaporation	100 (100)
5	*Project management*		*100 (100)*
5.1	Management	Continuous action, reporting finished but delivered behind schedule	100 (100)
5.2	Exploitation	Continuous action, selling started, TIP made but delivered behind schedule	100 (100)

5. MANAGEMENT AND CO-ORDINATION ASPECTS

The overall performance of the consortium in the programme was good. The co-operation between the partners in the project was well established from the beginning. Especially the small amount of partners in the project has made it possible to make fast decisions. All partners were very well dedicated to the project and the focal point, being the development of membranes, modules and systems to come to a quick implementation of tubular inorganic membranes in dewatering pervaporation processes in the process industry as a cost effective and energy efficient alternative for e.g. distillation was a very clear way mark for all partners from the beginning. The balance between fundamental research and insights, application and product development and final industrial production and use of the membranes was good.

A lot of information has been exchanged and the different partners have sent relevant information around. Especially on module design extensive information exchange between Aachen and Sulzer have taken place, by email, phone and in bilateral meetings. On the membrane stability there was continuous and regular update between ECN and Sulzer and every 2 months a meeting was held to discuss the progress. Two technical employees of Sulzer have twice visited ECN for several days in order to study and learn the membrane preparation procedure from ECN. An employee of ECN has visited Sulzer in spring 2003 for several weeks in helping to debug the production plant at Sulzer.

Haltermann has decided to abandon the project on 1 February 2002. Since the mid-term meeting the only communication with Haltermann was on management level (on how to deal with leaving the project). Because of extensive search a new end-user - Lyondell Chemical - has been found offering their facilities for testing on location. Cooperation with Lyondell has been very good and has led to successful experimental results, even though they were formally no part of the consortium.

At RWTH Aachen a change of PhD student working in the project has taken place but as the new PhD student Dipl.-Ing. M. Schleger was involved in the project from the start, he could take over the work from Dr. S. Sommer very smoothly.

Most of the reports have been delivered too late. Part of this is explained by the choices made due to the withdrawal of Haltermann. Mainly by the late signature of the amendment and partly by the long time the coordinator had to use to prepare a well readable report that fits the guidelines of the Commission.

Yearly progress meeting and half year update meetings have been held in which detailed progress has been discussed. During the mid-term meeting the project progress has been presented to the scientific officer.

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6. RESULTS AND CONCLUSIONS

The recipes and technology of preparing the microporous silica membranes for pervaporation have been scaled up. It has been shown that the technology of manufacturing considerable size high quality tubular microporous silica membranes on commercially available alumina supports (length of 1 metre, outer diameter of 14 mm) is possible. These commercially produced membranes have a good performance in pervaporation and show similar results as the membranes prepared on lab scale. Some debugging of the full-scale coating procedure is, however, still needed. The production capacity of the membrane manufacturing system and the peripherical manipulation has been designed for an output of 12,000 membrane tubes annually. Dewatering of aprotic solvents by pervaporation is possible with these membranes, which is not possible with commercial polymeric membranes. The acid stability is better than commercially available zeolite A membranes but it needs improvement.

Lab scale testing of the membranes has been performed for pervaporation using several feed mixtures. In general the membranes perform very well in dehydration. The fluxes are much higher than reported for polymeric membranes and the water purity of the permeate meets the demands. The dewatering of tertiary butyl alcohol, A-fuel and propylene glycol have been selected as processes to be tested with a pilot scale unit. These processes have first been tested extensively on lab scale and show good results for both flux and selectivity. Pilot scale testing of these processes using a 1 m^2 membrane area test installation based upon inorganic membranes has shown that dewatering of A-fuel on pilot scale even leads to higher selectivities than on lab scale: good fluxes were combined with more than 90 wt.% water in the permeate. For the A-fuel mixture on pilot scale fouling of the membranes occurred due to deposition of minerals from the tap water used. Lab scale testing has shown that this fouling does not occur in vapour permeation mode, though the selectivity in vapour permeation is somewhat lower than for pervaporation. In the propylene glycol mixture testing the selectivity of the membrane in 1 m^2 testing was lower than as measured on lab scale (very high selectivities), due to some defects in the membranes. For A-fuel and propylene glycol dewatering energy savings are respectively 60% and 36%. For the TBA process the price increase for the TBA product due to the use of the pervaporation membranes is 3.5€ per ton of TBA sold, which is less than the daily fluctuations of the market price. For A-fuel the economics of the process are not favourable. For the glycol production process the investment in the membranes will be paid off by the capacity increase within one year. As a reference process dehydration of iso propyl alcohol was investigated and for this process investment and operation costs are reduced by more than 40% and energy savings up to 85% could be achieved for pervaporation compared with a conventional distillation process. Furthermore the process of producing lactic acid has been optimised by incorporating inorganic dewatering membranes in the process.

During testing the silica membranes, a water flux decline of about 50% in the first few days was observed in combination with a further slow decline of the flux over longer time. The problems and results on this flux stability are now being reported in literature by some universities, though measurements have been performed only for days and no clue is given on solutions for the flux decrease in time by them. First insight into the mechanisms behind the flux decline has been obtained in this project. By incorporating methyl groups in the silica structure the initial flux decline has almost disappeared and the methylated silica membranes almost meet the first set of criteria for long-term industrial implementation. The membranes can, for the moment, only be used in dewatering up to a temperature of 100°C as at higher temperatures (e.g. 165°C) the membrane looses its selectivity after less than 50 days of continuous pervaporation testing. The solution of working with methylated silica membranes has been reported once elsewhere. The new problem of loss of selectivity at high temperatures has never been seen before for these membranes and has not been reported anywhere as probably nobody is yet able to perform these measurements.

The technical difficulties of high temperature sealing of ceramic membranes in a module of a size of 1 m^2 have been solved and can be used in industrial scale modules as well. This is a very big step forward as in general, even on lab-scale, sealing has shown to be difficult and hardly possible at high temperatures and in aggressive media. A good understanding of both the necessary hydrodynamic conditions and module configurations has been obtained, which will ensure optimal operation of the membrane module and system. Calculations on heat transfer in the isothermal membrane module and pressure drop on the feed side have been combined with calculations on module arrangements. Optimisations for module arrangements in combination with the processes have been suggested. These have been combined with costs optimisation of a membrane system as a function this arrangement, which showed that the membrane costs are much higher than the feed pump costs. It has been shown that modules in series in general leads to lower costs than modules (partly) arranged in parallel. Furthermore it was shown that steam heating of the isothermal SMS® module is much more efficient than using thermal oil for heating. Based upon chemical engineering and computational fluid dynamics calculations the pressure drop of the SMS® membrane module has been minimised. Several modules (single tube, two membranes, up to a module with 5 m^2 of membrane area) have been made and designs for larger scale modules are available.

The results will be implemented on a larger (pilot plant) scale. End-users from the (petro)chemical, oleochemical and pharmaceutical industries have main interest in up-scaling and using the technology on full scale in their processes. Furthermore they aim at the development of new chemicals and advanced process-routes using the results of this project. From the hardware point of view (membranes and modules) a manufacturing plant is in the start up phase. Selling membranes, modules, and systems for application in separation processes in applications fields as wide as possible has started as well. Because of the project results the membrane producer and membrane system developer Sulzer Chemtech will world-wide be the first company that commercially produces microporous silica membranes for dewatering that have proven to work under different processes. A first pervaporation plant based upon the methylated silica membranes has been ordered from Sulzer.

The above status can be considered as the most advanced global state of the art. The membranes are produced commercially and operation in the first commercial plant has started, which is a new state of the art. Probably others will use these membrane and module performances as a standard for comparison.

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