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REDUCTION OF ENERGY CONSUMPTION IN THE PROCESS INDUSTRY BY PERVAPORATION WITH INORGANIC MEMBRANES: TECHNO-ECONOMICAL FEASIBILITY STUDY

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Revisions	
A	Final version of the final publishable report of project 'Inorganic membrane pervaporation': JOE3-CT97-0074
B	

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Preface

The research described in this report is the publishable summary of a project that was partly financed by the European Commission (project number JOE3-CT97-0074) and carried out jointly by the Netherlands Energy Research Foundation (ECN), Institut Français du Pétrole (IFP), Akzo Nobel and RWTH Aachen. This project has been performed in the period Jan. 1998 up to Dec. 2000. The work performed by ECN was also partly funded by NOVEM B.V. under NOVEM contract number: 333105/0145 with the original title "Reductie van het energieverbruik in de procesindustrie door pervaporatie met anorganische membranen: technisch-economische haalbaarheids studie" and in part funded by ECN's 'Samenwerkingsfinancierings' (co-operative funding) programme.

Abstract

The aim of the project was to study the possible reduction of energy consumption in the process industry by using inorganic pervaporation membranes. This was done by evaluating the technical and economic feasibility of these membranes for dewatering, thus enhancing a quicker implementation of the membranes and membrane technology. The microporous silica and silicalite membranes should replace energy intensive distillation processes for the separation of liquid mixtures. The project focussed on four process cases: i) ether production, ii) extraction of aromatics from gasoline, iii) ester production and iv) dewatering of solvents. These processes are representative for a large group of applications in different fields of industry. The project consisted of four main activities:

1) membrane manufacturing
2) module design, development and optimisation
3) membrane and process testing on laboratory and bench scale
4) process calculations, optimisation and evaluation by flowsheeting.

Microporous silica membranes can be produced on a large scale and have shown to be able to separate effectively water from various organics by means of pervaporation. A new type of silica membrane has been used in the project to separate methanol from MTBE and toluene and ethanol from ETBE. The stability of the membranes in acid environments is good but should be improved further to enlarge the field of applications.

Modules based on tubular ceramic membranes with a silica top layer have been made on lab scale (1-tube) and on bench scale: 7 tubes with a diameter of 14 mm and a length of 40 cm. Detailed designs of a full-scale (5 m^2) module and a design of a 50 m^2 module have been made. The modules can be used up to 300°C and 25 bar pressure. The total price is governed by the module price and not by the membranes, assembly or sealing.

From the techno-economic evaluation studies several conclusions have been drawn for the different processes. For the separation of methanol from MTBE pervaporation can not compete with catalytic distillation as membrane selectivities are too low, costs are too high and the conventional process is more energy efficient than the hybrid (combination of distillation and pervaporation) flowsheet. Reduction of benzene in gasoline via pervaporation is not possible thus far, because of the very simple and cheap base case and low membrane performance.

Membrane pervaporation to separate EtOH from ETBE in the ether production process leads to about 30% lower costs for ETBE. The reduction in energy consumption for the whole process is between respectively 21 % and 37% when simple distillation or catalytic distillation is replaced by membrane pervaporation. Dehydration of the ethanol recycle by pervaporation increases the catalyst life time, leads to less by-products and a better water wash operation.

In Europe 19 PJ/year can be saved when esterification processes are assisted by pervaporation in stead of distillation. The production costs for esters by an esterification process based upon pervaporation are 30% lower than in using the distillation process. The use of pervaporation membranes for dewatering in esterification reactions furthermore results in a much better product quality, compared to normal distillation and to an increased reactor efficiency. The energy use is only 16% of the total energy use in the conventional distillation process.

The dewatering of isopropanol (IPA) by a hybrid distillation + inorganic pervaporation membrane process is about 40% cheaper than the conventional distillation case and requires up to 70% less energy than the distillation process. The energy savings in Europe for IPA production could be up to 2 PJ/year. When IPA recycle streams are included, the energy savings in Europe could be as high as 10 PJ/year.

Following the results of the project the technology of producing microporous silica membranes for dewatering has been licensed to Sulzer Chemtech, world-wide leader of polymeric membranes and membrane systems for pervaporation. Sulzer will produce and sell the membranes, membrane modules and technology on a commercial basis.

Keywords

Pervaporation, Ceramic membrane, Energy efficiency, Process design

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1. INTRODUCTION

1.1 Objectives of the report

The objectives of the project were to study and evaluate the feasibility of inorganic membrane technology in pervaporation processes for application in the process industry in order to reduce drastically the energy consumption by substitution of conventional separation processes like distillation. The specific aim was to enhance the implementation by showing that the claimed benefit exists. Furthermore to show that inorganic membranes are reliable, and that their use leads to cost-effective separation processes, which are technically feasible. The project focuses on four cases in the following application fields: i) ether production, e.g. MTBE and ETBE ii) extraction of aromatics from hydrocarbons iii) ester production, with diethyltartrate as a model esterification and iv) dewatering of solvents. Both tubular microporous silica and silicalite (zeolite) membranes are used, depending on the separation to be performed.

The most important measurable technical objectives/achievements were:

- To give an overview of the technical and economic feasibility of a combined pervaporation process based on inorganic membranes and the production of valuable chemicals like ETBE (Ethyl-Tertiary-Butyl-Ether) and esters and the separation of aliphatic and aromatic hydrocarbons and the dehydration of organics, including a description of the path to be followed to come to pilot plant scale testing and/or commercialisation.
- Give estimations of the total system efficiency in terms of energy use and cost-effectiveness; comparison with existing processes.
- Experimental results (laboratory and bench-scale) concerning the permeability, selectivity, and stability of inorganic membranes in these processes. The data will be used to determine the process parameter envelopes and to make optimum process designs.
- Optimal module designs, constructions, and reactor concepts.
- Optimal process configurations for the various applications.
- Pre-designs of energy efficient pervaporation processes based on inorganic membranes by a combination of unit operations like chemical reaction, separation and heat exchange.
- Estimations of the environmental advantages.
- Insight in the improvement of product quality.

2. TECHNICAL DESCRIPTION OF THE PROJECT

Pervaporation is the selective evaporation of one component of a liquid mixture via a membrane, which is in direct contact with the liquid mixture. Because of this, a much more energy efficient process can be obtained compared to distillation, in which all components are evaporated. Even difficult separation of azeotropic mixtures can be performed in one step. Thus, the (partial) replacement of distillation by pervaporation or the combination of pervaporation and reaction in one unit operation will have important benefits with respect to energy consumption, yield, product quality, and size of down-stream process equipment. New microporous membranes based on hydrophilic silica for the dewatering of organic solvents are a promising candidate for these separations. In contrast to the polymeric membranes the silica membranes can be used above 100^{o}C, even up to 300^{o}C.

The approach is based on a combination of:
- availability of applicable inorganic membranes,
- inorganic membrane manufacturing and optimisation expertise,
- detailed knowledge of separation and pervaporation processes, and,
- process know-how on the relevant chemical production processes.

The processes studied in detail have been selected to be representative for a large number of analogous processes in different fields of industry, that may benefit from the application of inorganic pervaporation membranes. These are:
- *Ether production***.** MTBE, ETBE and TAME are considered as examples for an organic/organic (also polar/non polar) separation in etherification processes.
- *Extraction of aromatics***.** Benzene separation from a hydrocarbon mixture in catalytic reforming are studied as an application in the petrochemical and refining industry.
- *Ester production***.** The esterification process of tartaric acid with ethanol to diethyl tartrate is taken as an example of numerous equilibrium reactions. Water removal from the reaction mixture will increase the yield and product purity by shifting the equilibrium. It serves as an example for the coupling of a membrane separation process and chemical reaction without extensive loss of alcohol or extra formation of side products.
- *Dewatering of solvents***.** No selection for a particular case has been made at the start of the project. A number of examples have been screened theoretically and experimentally in order to define the range of conditions under which pervaporation with inorganic membranes will lead to substantial energy savings and specific advantages. Isopropylalcohol (IPA) dehydration has been worked out as model cases, including a parallel cost and energy comparison for conventional and pervaporation processes.

The work comprised detailed technical and economic evaluations of the feasibility of pervaporation with several types of inorganic membranes by a combination of experimental laboratory and bench-scale studies i.e. membrane, reactor/separator and process testing, process and reactor modelling, system integration and design studies.

With respect to the membranes, the first focus was on tubular silica membranes, which are available on a sufficient scale, in a high quality and in proper modules. Zeolite (silicalite) and modified silica have been explored as well. Process specific inorganic membrane development and optimisation has been performed. Aspects such as membrane performance (flux, selectivity) in the specific applications, durability, producibility and full-scale chemical process pre-designs have been covered. Finally energy savings and costs reductions as compared to conventional options have been addressed. A database on general inorganic membrane pervaporation characteristics is obtained and an overview of the possibilities in other processes was made.

Specific for the dewatering of solvents it is impossible to select just one case, which is typical. Energy requirements of distillative dewatering vary so much that a single example will not be convincing. A number of water/solvent separations have therefore been studied. Energy consumption and economic advantage of pervaporation has been calculated for the dehydration of isopropanol as a function of water concentration and purity requirements.

In the next schedule an overview of the project management structure and tasks is given. The following abbreviations are used: ECN = Energy research Centre of the Netherlands, IFP = Institut Français du Pétrole, AKZO = Akzo Nobel, Aachen = RWTH Aachen, and Mulhouse = Univ. of Mulhouse (subcontractor to IFP).

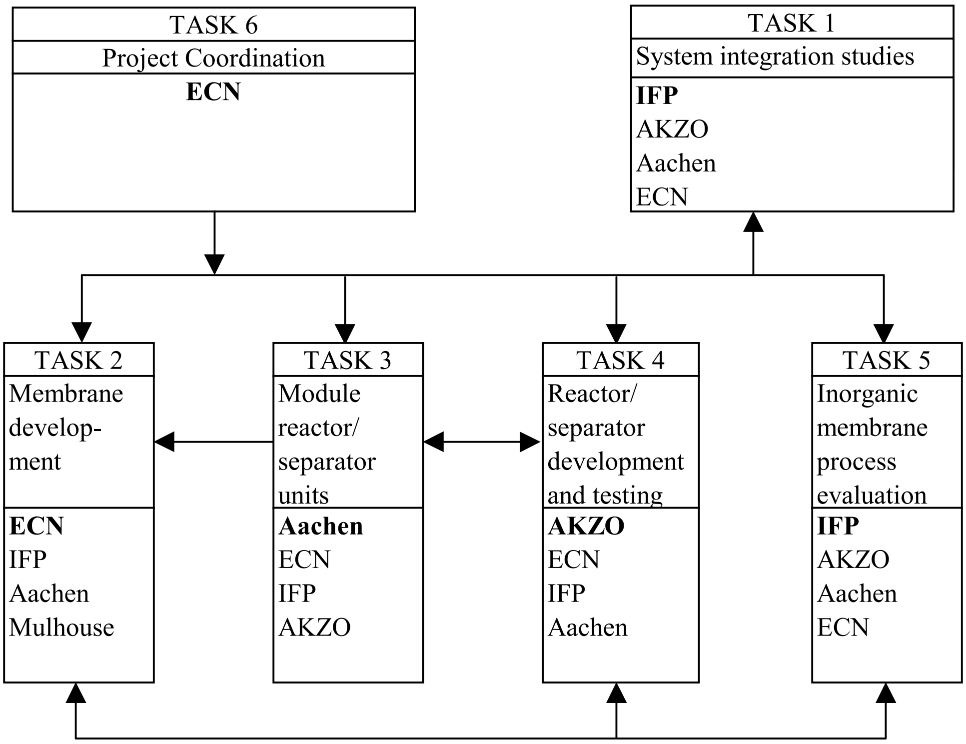


Figure 2.1 *Project management structure and tasks in the project*

Task 1. System integration studies

Purpose of the system integration studies was to get insight into the economics of the processes comprising inorganic pervaporation membranes vs. conventional production processes, including the use of polymeric membranes. The overall efficiency of the processes was determined. Process schemes have been developed.

Task 2. Membrane development

The aim of this task was to test the functionality and performance of the membranes before going into the extensive reactor test programme and to obtain a generic set of inorganic membrane characteristic as pervaporation membranes.

Task 3. Module and reactor/separator units

The goal of this task was to design and build (computational) models and modules for assistance in the experiments and for making pre-designs of full-scale reaction/separation units.

Task 4. Reactor/separator development and testing
In this task the technical feasibility of the novel membrane pervaporation processes was demonstrated on a bench-scale. Representative bench scale reactors/separators have been designed and constructed according to the most promising configurations. Bench-scale experiments have been performed. Data concerning reactor/separator performance were used for the drafting of a preliminary full scale process design.

Task 5. Inorganic membrane process evaluation
The studies define the required extent of reactor conversion and/or separation efficiency. From system integration studies the boundary conditions for the chemicals production process development have been defined and the consequences for the overall system were elaborated. Different configurations of combinations of unit operations have been considered. Each configuration has its specific (dis) advantages resulting in different specifications for the membrane reactor/separator unit and overall efficiency.

3. RESULTS AND CONCLUSIONS

3.1 Membranes and basic performance

Microporous hydrophilic silica membranes, see Figure 3.1 that can be produced on a larger scale have shown to be able to separate effectively water from various organics by means of pervaporation. The separation performance in terms of permeate flux and selectivity is graphically shown in Figure 3.2 (in most cases: feed 10 wt.% water and 10 mbar permeate pressure). More than 100 of these membranes varying in length between 20 and 80 cm have been produced. A typical and reproducible performance for all these membranes is that for the separation of 5 wt.% water from butanol at 75°C and 10 mbar permeate pressure the water flux is about 3.6 kg/m^{2}h and the permeate contains about 98 wt.% water.

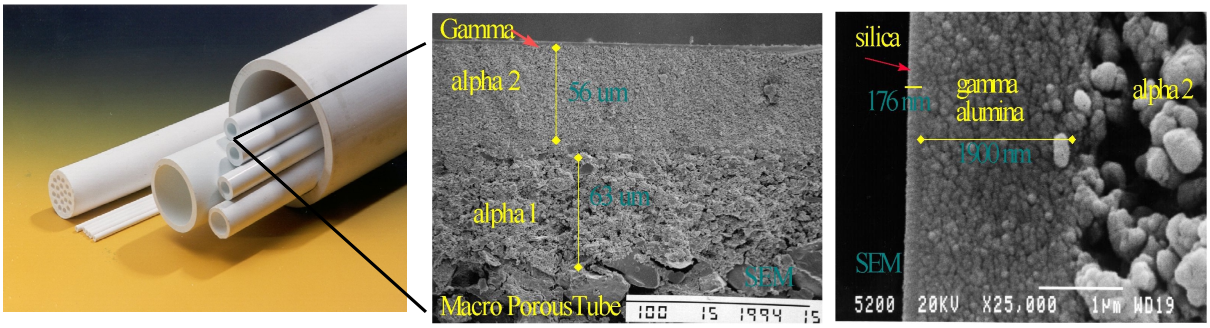


Figure 3.1 *SEM micrographs of silica membranes and membrane layers*

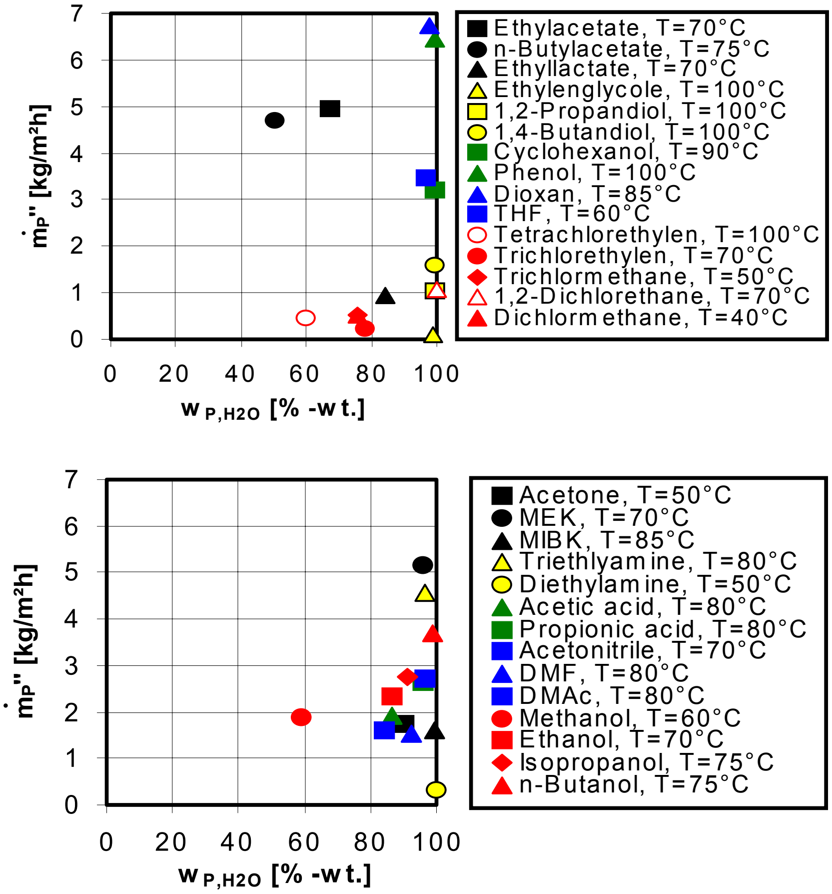


Figure 3.2 *Total permeate flux over water concentration in the permeate*

The inorganic membranes can be used at higher temperatures than the polymeric types and the fact that the flux and selectivity improves with increasing temperature makes the silica membranes much better candidates in process applications. Tests have been performed up to 240°C. The long-term stability of the membranes should be tested more extensively and the stability in acid environments should be further improved.

Zeolite (silicalite) membranes have been prepared with a low defect density and showed good selectivity in alkane/isoalkane separation. However, these membranes exhibit low selectivity for the envisioned separation of alcohols from ethers and benzene from gasoline. Therefore a new type of silica membrane with a more hydrophobic character than the 'standard' silica has been used in the project. These membranes can separate methanol from MTBE and methanol from toluene very well and ethanol from ETBE with a somewhat lower flux and selectivity. For the separation of 4 wt.% methanol from MTBE at 45°C and 10 mbar permeate pressure the MeOH flux is about 1 kg/m^2h and the permeate contains about 95 wt.% MeOH. These membranes have been used in the process studies for the separation of organic liquids.

3.2 Module design and price

The performance of practical membrane modules containing large surface areas is lower than the ideal membrane performance. This is due to the fact that one component (water) is permeating through the membrane causing a lower concentration of this component near the membrane surface. Furthermore, this component is evaporated for which the heat is taken from the feed. The lower the concentration and the lower the temperature, the lower the flow through the membrane will be. These effects are called concentration and temperature polarisation. Consequently, with inorganic high flux membranes, module design becomes very important to overcome these effects. On the other hand there is little choice in module concept, since inorganic membranes can best be manufactured in tubular form. Calculations and modelling (by chemical engineering calculations (CEC) and Computational Fluid Dynamics (CFD)) show that the perpendicular flow increases the flux through the membranes. Baffles should be used for promoting a well-defined perpendicular flow in a 7-tube bench scale module, Figure 3.3. This module has been designed, and 3 of them have been made and tested. Optimisations have been performed by CEC and CFD, see Figure 3.4 and 3.5.

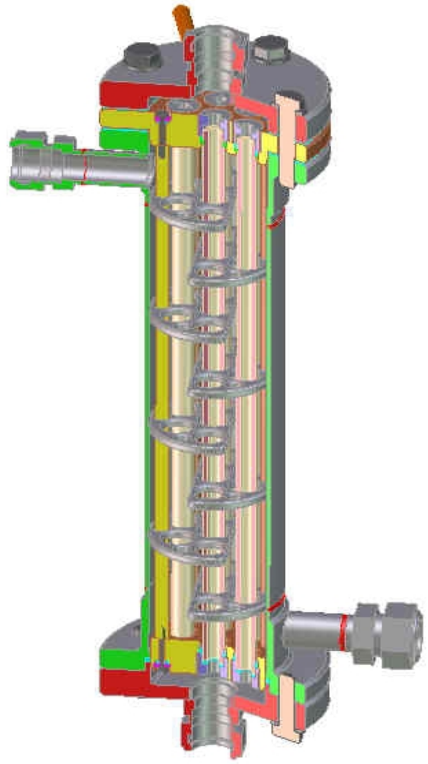
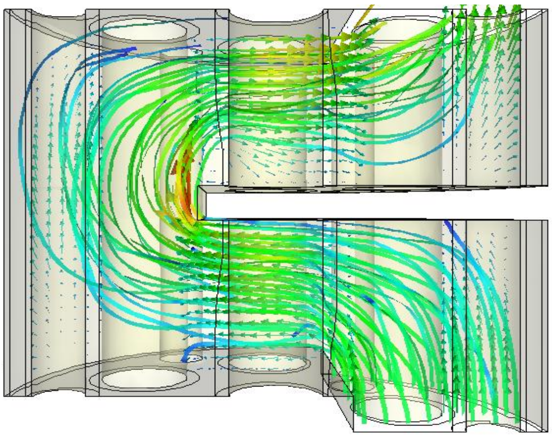


Figure 3.3 *Bench scale module*



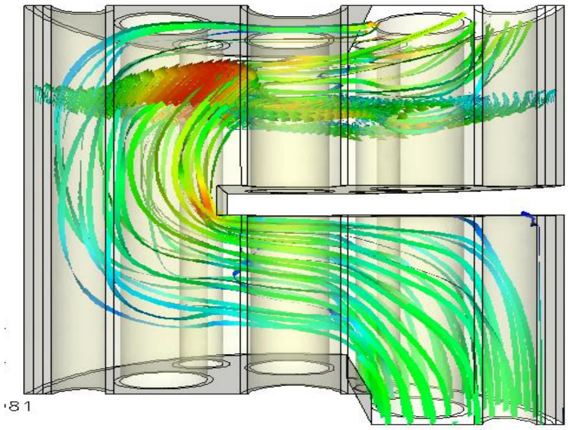


Figure 3.4 *(left) Streamlines and vectors depicting flow pattern in bench-scale module*
Figure 3.5 *Flow pattern prevailing in a membrane pervaporation module optimised by CFD*

Experiments show that with the bench scale module the same flux through the membranes can be obtained with a 5 times lower feed flow (relative to the membrane surface area) as in a 1-tube lab scale module. So, much less energy-input is needed to obtain the same performance. Furthermore, the concept of sealing to overcome the difference in thermal expansion between the stainless steel module and ceramic tubes at high temperature has proven to work well. Design calculations (lab and bench scale) by Chemical Engineering Calculations (CEC) and Computational Fluid Dynamics (CFD) correlate well with experimental results and it has been proven that the CEC models can be used for optimising a full-scale module. An optimised geometry of a full-scale (5 m^2) module has been made and a preliminary design of a 50 m^2 module has been made. Some calculations on this design are presented in Figure 3.6. Based upon this final design and the available methods and models, modules with other membrane surface areas can be designed.

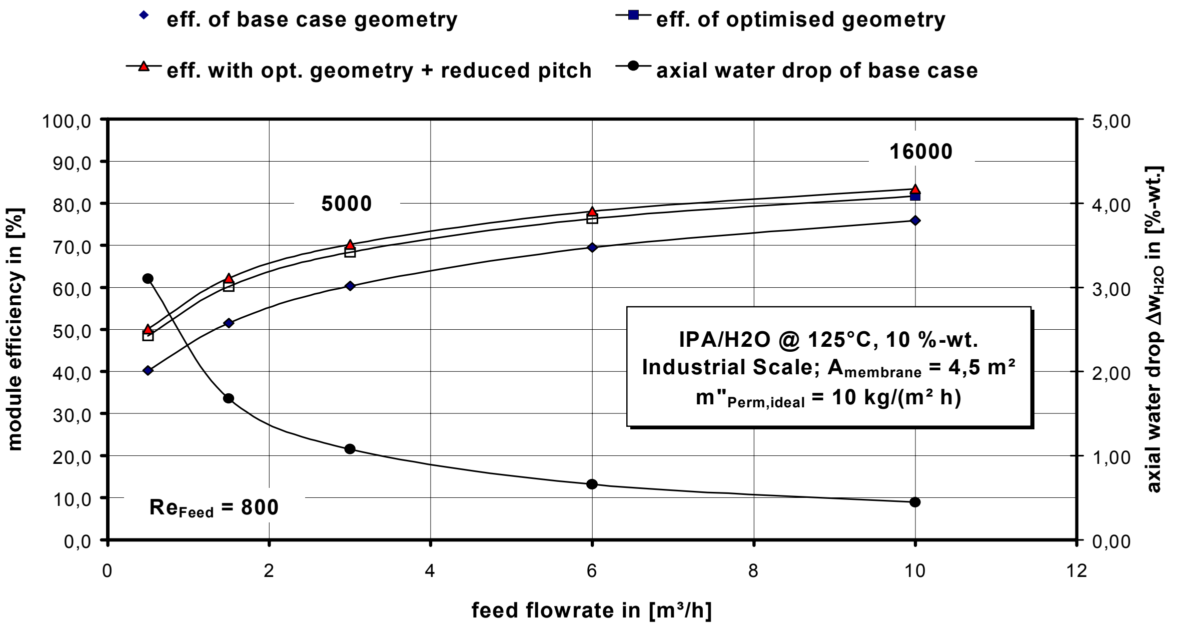


Figure 3.6 *Influence of module optimisation on module performance*

As illustrated in table 3.1, the total price of the membrane module is governed by the module price (meaning the steel and manufacture price) and not by the membranes, assembly or sealing. Therefore cost optimisation should mainly focus to the module itself and not to the membranes. This also proofs that the often heard statement that ceramic membranes are much more expensive than polymeric membranes is only valid for the inorganic membranes themselves and not for the complete module.

Table 3.1 *Membrane and module pricing for module concept with baffles*

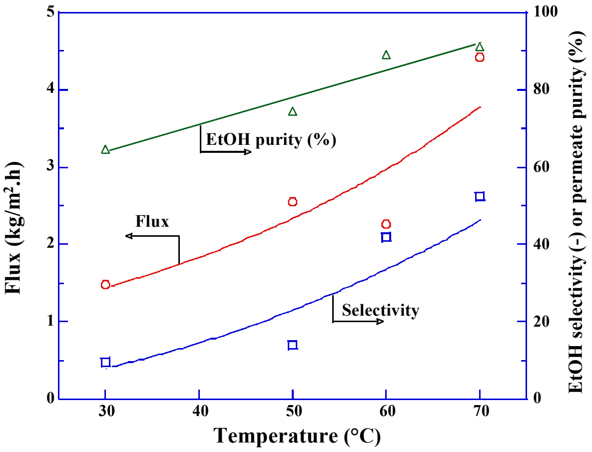
Area	Seal + Membr.+ Assembly	Seal + Membr.+ Assembly	Total module price	
[m^2]	[Euro]	[Euro/m^2]	[Euro]	[Euro/m^2]
1	1,580	1,580	10,650	10,650
5	4,140	828	21,160	4,230
10	6,280	628	25,140	2,510
25	10,880	435	34,020	1,360

3.3 Process development, testing and evaluation

3.3.1 Ether production

The selectivity of hydrophobic silica membranes for the separation of methanol from MTBE has been measured in methanol-MTBE mixtures at different concentrations and temperatures. The results show that the selectivity is too low compared to the targeted membrane performances. Cost calculations using the measurement results and also assuming higher selective membranes show that pervaporation can not compete with catalytic distillation, as large membrane surface areas are required to purify MTBE. The reduction in investment needed requires very low membrane costs (below 20 Euro/m^2), which is absolutely not feasible (compare with table 3.1), and higher membrane selectivities. The hybrid process has a higher energy consumption than the conventional process. Due to environmental issues the addition of MTBE to gasoline will probably be forbidden world-wide as MTBE is toxic, slight solubility in water and has a low biodegradability. Currently there is no clear understanding of the market for MTBE and the implementation strategy.

In the ETBE processes there are 2 possibilities to implement pervaporation: water separation from ethanol and ethanol separation from ETBE. In the first option pervaporation is used to further dehydrate water from the water wash section. With less than 10 m^2 of silica membrane area one obtains ethanol with less than 1 % of water, which is the requirement. Although the hybrid pervaporation process consumes more energy and requires extra investments, the hybrid process increases the operability of the water wash section's, and the lifetime of the resin catalyst. So it can be an attractive solution to the operators. In the second process option, which has been extensively studied during the project, the pervaporation assists the ETBE purification, removing ethanol from a side draw of one of the distillation columns (the debutaniser). The separation demands are set to a selectivity of 70 and an ethanol flux of 2.5 kg/m^2h at 20% EtOH in the feed and a temperature of 80-120°C. The hydrophobic silica membrane performance meets these demands for the separation of ethanol from ETBE, see Figure 3.7 and 3.8. Flowsheeting calculations show that a hybrid membrane pervaporation and distillation process for ETBE production leads to energy savings of up to 37% compared to the conventional process. This figure increases if one compares only the purification part of the process, reaching from respectively 52 % up to 55 %. This energy saving is mainly due to the fact that the two distillation columns, that in general use a lot of energy are replaced by a much more energy efficient pervaporation process. Furthermore the costs of producing ETBE are about 30% lower, see Figure 3.9. Such interesting conclusions remain valid also for different plant capacities, conversions or membrane prices. However, the market for ETBE is not clear and the ETBE purity specification is difficult to forecast. Some alternative strategies to produce pure ETBE (for example to accept to produce ether with a low conversion) could also mean that implementation will not go forward.



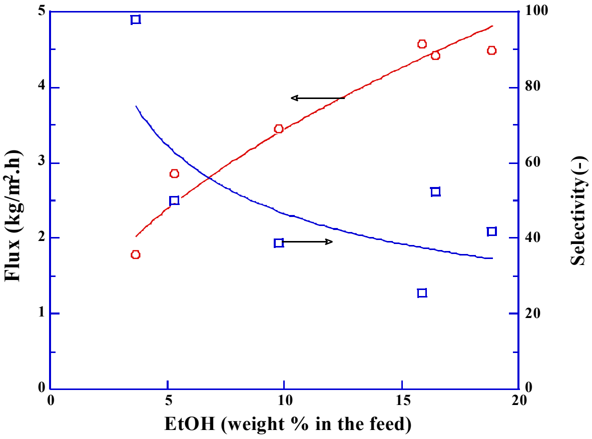


Figure 3.7 *(left) Influence of temperature on modified silica membrane performances (purification of ETBE). Feed: 240 L/h – 16% EtOH / 84% ETBE- $P_{perm.}$ 3 mbar*

Figure 3.8 *(right) Influence of feed content on modified silica membrane performances (purification of ETBE). Feed: 240 L/h - 70°C - $P_{perm.}$ 3 mbar*

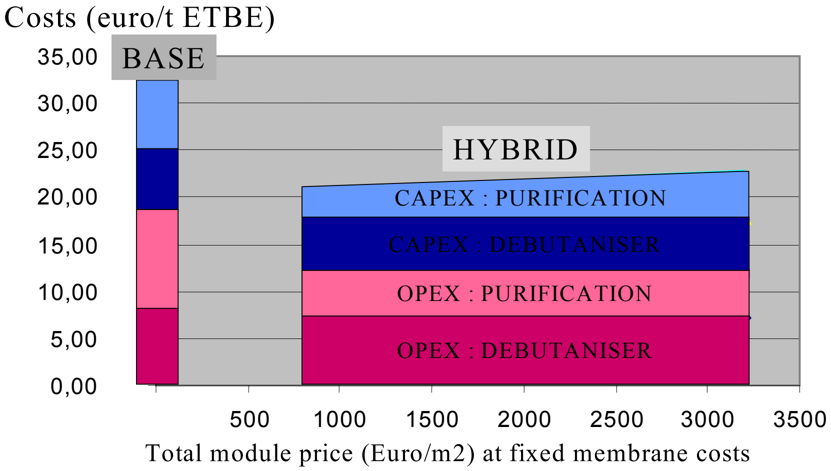


Figure 3.9 *Influence of membrane module costs on ETBE production costs*

3.3.2 Extraction of aromatics

Benzene reduction from the gasoline pool with pervaporation requires high investments and operating costs. The calculations made on a feed corresponding to a typical full-scale process revealed the need of a large membrane surface. The costs for this represents more than half of the total investment including the naphtha splitter. Neither the membrane selectivities nor the product prices could affect significantly the competitiveness of the hybrid process. The important parameter is the membrane price (or membrane flux), which has to be reduced by a factor of 2 in order to obtain the same naphtha purification cost price as the conventional case. However, a further membrane cost reduction of 3 times is necessary to decrease the base case product price of about 5 %. This comes from the fact that the available base case is very simple, cheap and extremely difficult to compete with. Moreover, high permeable and selective membranes (polymeric or inorganic) to perform the separation are not available.

3.3.3 Ester production

For the esterification of tartaric acid to diethyltartrate the use of membranes results in a much better product quality and the product quality, compared to normal distillation, can be varied depending on the requirements. In the membrane case the reactor use is better (higher filling degrees as no boiling or foaming occurs) and high energy savings can be obtained. However, the membrane is not stable enough in this application due to the very strong acidic environment. Therefore a new esterification reaction has been added to the project. In this new combined esterification and pervaporation process, the increased reactor efficiency (less excess, higher filling degree) results in a production per batch which is twice the production in the distillation process. The water flux meets the project targets and the process selectivity is good, see Figure 3.10. Mainly because of the increased annual production, the production costs in the pervaporation process are 30% lower than in the distillation process. The costs of the membrane module are only a small part of the total production costs. The energy use decreases to only 16% of the total energy use in extractive distillation (per ton product), Figure 3.11. Energy savings in Europe can be up to 19 PJ/year for esterification processes in general. The production costs in the pervaporation process are 30% lower than in the distillation process. Membrane development aimed at a more stable and inert material is recommended so the membranes can be used in all (aggressive) esterification processes as well.

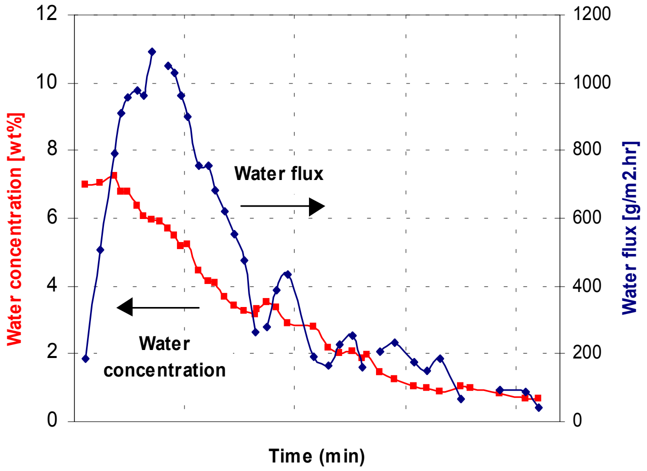


Figure 3.10 *Reaction/pervaporation experiments for esterification: water concentration in the feed and water flux through the membrane vs. time*

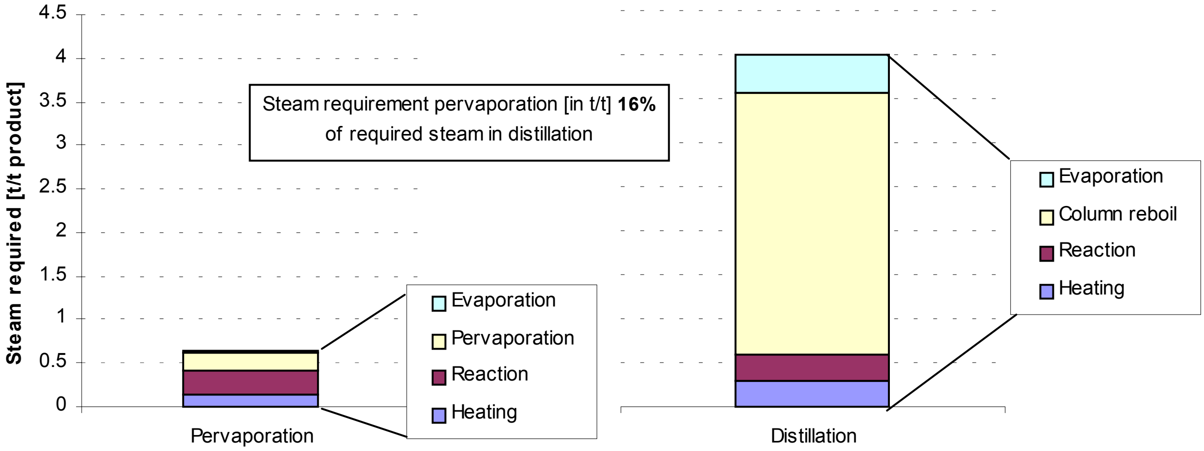


Figure 3.11 *Steam requirements reaction/pervaporation and for reaction/distillation*

3.3.4 Solvent dewatering

The dewatering of isopropanol (IPA) has been chosen as model for the use of inorganic pervaporation membranes in dehydration processes. Measurements on 5 wt.% water in isopropanol mixtures at 80°C using silica membranes show a total permeate flux of 3.0 kg/m^2h and a water concentration in the permeate of 97.6 wt.%. Important aspects that have been accounted for in the technical and economic evaluation are the temperature drop in the module due to the heat of evaporation of water and the amount of modules, heat exchangers and piping necessary to minimise this problem, see Figure 3.12. In the extreme case that only 1 membrane module is used for the separation, so no (interstage) heating of the feed liquid is possible. Therefore the temperature drop will be significant and thereby, as the flux decreases with a temperature decrease, a large membrane area is necessary to perform the separation. However, the amount of modules, piping, etc. is small so the costs of the equipment are relatively low. In the case of using several (smaller) modules in series, interstage heating can be used and the temperature drop is low. So, the membrane area needed is much smaller than in the case of using only one membrane module. But, a lot of extra piping, heat exchangers, etc. are necessary, so the costs are high. The influence of the permeate pressure on the costs and membrane area needed have been studied as well, see Figure 3.12.

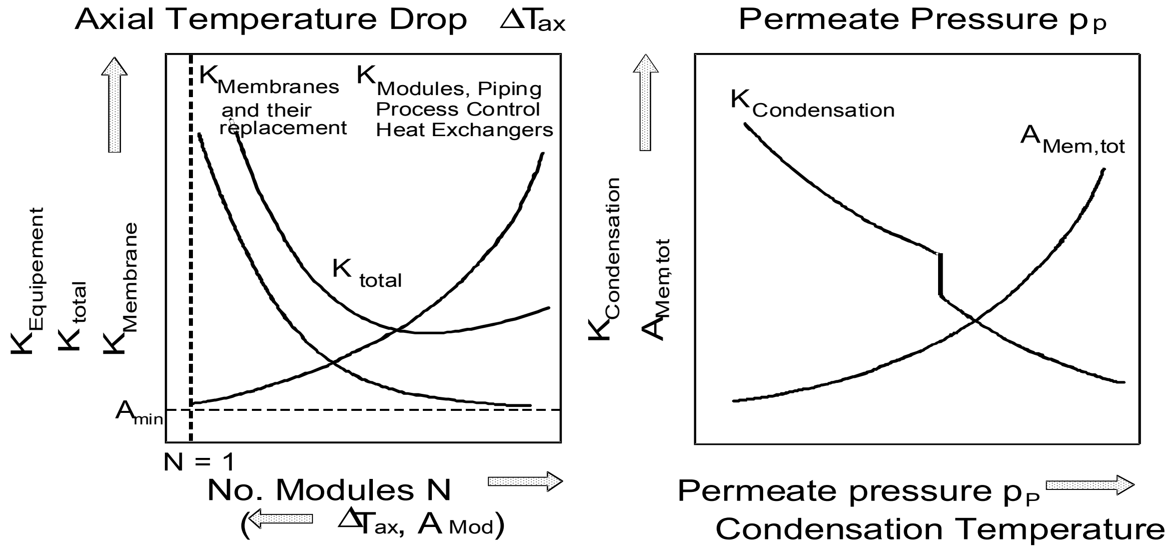


Figure 3.12 *Relative influence of several parameters on costs*

Three membrane cases were studied: 1. Polymeric membranes to break the azeotrope between the two distillation columns, 2. Ceramic membranes in the same process configuration, and 3. Ceramic membranes as a stand-alone process. All cases are about 40% cheaper than the conventional extractive distillation case, see Figure 3.13. Furthermore the inorganic membrane case is about 7% cheaper than the polymeric membrane case. A stand-alone process based upon silica membranes is more expensive than the hybrid process as more membrane area is needed, but it is still about 30% cheaper than the conventional process. The hybrid pervaporation and distillation process requires up to 70% less energy than the distillation process. The energy savings in Europe could be up to 2 PJ/year for the production of IPA. Taking IPA recycle stream dehydration into account energy savings in Europe could be as high as 10 PJ/year. The potential value for making new products with this technique is 100 MEuro. In more than 100 applications a potential of more than 50,000 m^2 membrane area can be found.

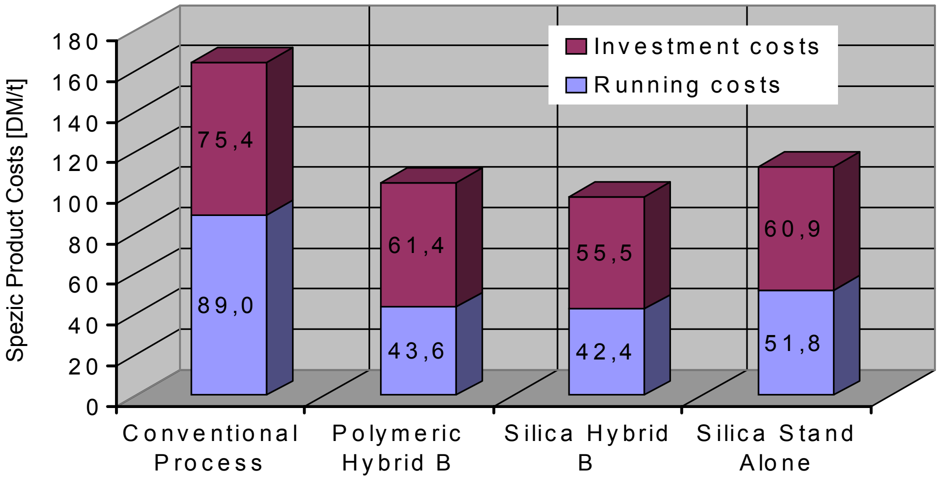


Figure 3.13 *Cost evaluation for conventional IPA dehydration vs. membrane options*

3.4 Summary on technical and economic feasibility and energy consumption

In the project a total of six processes with several different process options have been evaluated on the technical and economic feasibility of using inorganic membrane pervaporation. In the table below a summary is given on the feasibility of the membrane processes and the possible energy savings.

Table 3.2 *Advantages of inorganic pervaporation membranes in different processes, economic feasibility expressed as product cost price reduction*

Process	Technical feasibility *	Economic feasibility	Energy savings
MTBE	The hydrophobic silica membrane performance is good enough	The membrane option is not competitive against the existing technologies. The market unclear	No
ETBE Case A Case B	The hydrophobic silica membrane performance is in both cases good enough	28 % lower 31 % lower The market is unclear	21 % 37 %
EtOH in ETBE	The silica membrane performance is OK	Site dependant	No
Benzene in gasoline	Inorganic membranes for this separation are not available	The membrane process is not competitive	No
Esterification	The silica membrane performance is good, however, the stability should be improved	9 % lower	70 % and up to 19 PJ/year in Europe
IPA	The silica membrane performance is good	40 % lower	70 % and up to 2 PJ/year in Europe (10PJ/year incl. recycle streams)

* The membrane performances match with the process requirements but ageing tests need to be done in all cases in order to test the long term membrane stability

4. EXPLOITATION PLANS AND ANTICIPATED BENEFITS

Main result
An important outcome of the project is that the industry became aware of the potential of the inorganic membrane pervaporation. Because of the project the ECN patented and owned technology of producing microporous silica membranes has been licensed to Sulzer Chemtech (Heinitz, Germany), world-wide leader of polymeric membranes and membrane systems for pervaporation. Sulzer will produce and sell the membranes, membrane modules and technology on a commercial basis. Sulzer will start the production of these membranes mid 2001.

Benefits
The results of the project show that dewatering by pervaporation with inorganic membranes can give high energy savings and cheaper processes compared to distillation processes. Furthermore, processes will be simpler, fewer by-products will be formed and throughputs can be increased. The results are of particular interest for the chemical, petrochemical and pharmaceutical industry. As the savings and product purity are main advantages for pervaporation compared to thermal separation technologies the potential is high, however, the non-mature technique and therefore acceptance of the industry and the reliability still to be proven are the challenges that follow and are given appropriate attention right now. The membranes and modules can be produced on such a scale that demonstration should start, first with simple dewatering processes followed by dewatering of ‘difficult’ mixtures and later organics-organics separations.

Exploitable results and plans
Detailed plans for exploiting the results are included in the Technology Implementation Plan of the project. In the table below a summary of the exploitable results, owners and intentions are given.

The partners in the project have signed a consortium agreement to arrange details on secrecy and exploitation of results of the project.

Exploitable result	Partners (result owners) involved	Exploitation intention	Summary of result
Production of microporous silica membranes, modules and systems for pervaporation	ECN	Joint R&D and product development Licensing Strategic partnership Exploitation via others	Microporous silica membranes have very good performance in dewatering of organics. They can be combined with or replace conventional distillation processes. The membranes have a much broader application field than polymeric membranes. The silica membranes are made in a tubular geometry, having lengths up to 1 meter. The coating techniques are developed so that semi-industrial scale production is straightforward. Membrane modules have been made up to 0.1 m^2, they have been tested and showed good performance under relevant conditions. Designs of modules of 1, 5 and 50 m^2 have been made. The market for the inorganic membranes will first be in rather simple (end-of-pipe) dewatering of organics, which is already a multi million Euro market. Much more potential is in the integration of the separation membrane with reactions, thereby making better products by cheaper production methods. The market should be opened and convinced via semi-industrial scale production and demonstration, followed by full-scale production. **By Jan. 1 2000, Sulzer Chemtech and ECN signed a licensing agreement to exploit this result.**
Development of combined reaction and membrane dewatering processes for ester production	Akzo Nobel	Business creation	A reaction/pervaporation system offers the opportunity to shift the reaction equilibrium in a very efficient way by selective removal of one of the reaction products. Especially in case of esterification with lower alcohols, pervaporation has advantages compared to conventional (distillation) technology: - avoiding the need to distillate large volumes or to separate the required excess of alcohol, - a reduction in energy consumption, - operating conditions are not limited by the boiling point of the mixture or the azeotropes. The result is a design of a kton-scale esterification process for a model system, using the combined esterification/pervaporation technology. This is based on experimental results (lab-scale and bench-scale), literature research and computer simulations. Furthermore, general rules are defined for the application of membranes and the design of reaction/ pervaporation technologies. The technology is also relevant for condensation reactions in general (equilibrium limited reactions). Condensation reactions are a significant group of reactions commonly found in the chemical industry. The estimated turnover (1990) in Europe of products of this type of reactions exceeds 4,000 MEuro per year. **Akzo Nobel will use the results in-house for business creation**

Exploitable result	Partners (result owners) involved	Exploitation intention	Summary of result
Process development of membrane pervaporation in the petrochemical industry: production of ethers	IFP	Licensing, Business creation	Oxygenate additives like ETBE and MTBE can replace lead compounds in gasoline. Nevertheless MTBE has been recently classified as potentially toxic and its future use is not clear in Europe. Methanol and ethanol are used in excess in the industrial full-scale etherification processes. Due to azeotropes in the distillation step, the removal of the alcohol excess is limited in the conventional processes and the final ether product can be contaminated by alcohol. A selection of hybrid processes for the production of ETBE and MTBE has been made, with alcohol extraction assisted by pervaporation. A pervaporation model was implemented in (ProII) flowsheet software that uses pervaporation results obtained with available inorganic membrane materials. Among a series of inorganic membranes, a modified silica membrane manufactured by ECN exhibited the most interesting separation performances on lab and bench-scale. A reduction of energy consumption is foreseen by operating a pervaporation-based process to enhance ETBE purity at industrial scale, compared to a distillation-based purification. In the case of MTBE, pervaporation does not lead to significant gain. **IFP will use the results in-house**
Aromatics extraction process from gasoline by membrane pervaporation	IFP	Licensing, Business creation	The objective of the developed hybrid process is to reduce benzene content of gasoline (down to 1% vol.) to meet environmental regulations. A hybrid process for the reduction of benzene content from gasoline was proposed and was compared to a conventional alternative that was representative to industrial solutions. The result is not exploitable for 2 major difficulties: 1) Lack of selective inorganic materials 2) High performing conventional flowsheet The only possibility for the membrane technology to compete with these alternative solutions is that they produce a pure (i.e. minimum 99 wt.% benzene) benzene flux, for commercialisation or alkylation processes. **No exploitation is foreseen.**

Exploitable result	Partners (result owners) involved	Exploitation intention	Summary of result
Models and methods for the design of membrane modules	ECN, Akzo Nobel, IVT Aachen	Licensing, Joint product development, Spin-off, Consultancy, In house use.	The results are models and methods to predict dynamic transport phenomena in membrane pervaporation modules for the design of modules on lab scale, bench scale, and full-scale size. Aspects like concentration and temperature polarisation, which occur simultaneously in the pervaporation module, have been dealt with. The models and methods are based on expertise knowledge of pervaporation, combined heat and mass transfer, boundary layer phenomena and low Reynolds effects. The improved CFD models for the design of membrane module are implemented in the commercial available CFD package CFX. This package is used by most of the European process industries. The developed models can be licensed to other users of the CFX package. However, they are used as in-house tools in first instance. The developed CFD technology and methods are also relevant for other mass and heat transfer problems in the process industry. **No commercialisation actions will be taken in the field of selling software, however, the models and knowledge will be used for consultancy and CFD services to others.**
Dehydration of IPA process streams	ECN, IFP, Akzo Nobel, IVT-RWTH Aachen	Licensing, Joint R&D and process development, Strategic partnerships, Exploitation via others	Hybrid processes for the dewatering of iso-propyl alcohol have been made. A pervaporation model was implemented in flowsheeting software (as Fortran code) that uses experimental pervaporation results obtained with available inorganic membranes. The membrane based hybrid processes that have been developed are: <u>i)</u> a pervaporation unit between two distillation columns to break the azeotrope, and <u>ii)</u> pervaporation for azeotrope splitting and concentrating up to the end purity (stand alone process). The costs for the conventional IPA dehydration process are compared with three membrane cases: 1. Polymeric membranes to break the azeotrope between the two distillation columns, 2. Ceramic membranes in the same process configuration, and 3. Ceramic membranes as a stand-alone process. <u>Ad. i.</u> The membrane case is about 40% cheaper than the conventional case. The inorganic membrane case is about 7% cheaper than the polymeric membrane case. The hybrid pervaporation and distillation process requires up to 70% less energy than the distillation process. On lab scale and bench scale the process has proven to work. <u>Ad. ii.</u> A stand-alone process based upon silica membranes is more expensive than the hybrid process, but it is still about 30% cheaper than the conventional process. <u>Future:</u> Pilot scale R&D and demonstration is needed for further implementation. In more than 100 other applications this new technology seems interesting with a potential of more than 50,000 m^2 membrane area. The current annual turnover value for new products can be up to 100 MEuro. **The intention is to demonstrate the new technology via a pilot demonstration unit. This pilot unit should be installed on an industrial site.**

5. LIST OF SYMBOLS AND ABBREVIATIONS

A_{mem}	Membrane area	m^2
CAAA	Clean Air Act Amendment	-
BuOH	Butanol	-
CEC	Chemical Engineering Calculations	-
CFD	Computational Fluid Dynamics	-
DMAc	Dimethylacetaldehyde	-
DMF	Dimethylformamid	-
EC	European Commission	-
ECN	Energy Research Centre of the Netherlands	-
EtOH	Ethanol	-
ETBE	Ethyl tertiary butyl ether	-
EU	European Union	-
$H\text{-}SiO_2$	Hydrophobic silica	-
IFP	Institut Français du Pétrole	-
IPA	Iso propyl alcohol	-
IVT	Institut für Verfahrens Technik	-
L	Length	m
m_p	Flux	kg/m^2h
MEK	Methylethylketone	-
MeOH	Methanol	-
MIBK	Methyl iso butyl ketone	-
MTBE	Methyl tertiary butyl ether	-
NRG	Nuclear Research and consultancy Group	-
Nu	Nusselt number	-
P	Pressure	Pa
PV	Pervaporation	-
Pr	Prandl number	-
Q	Flow	l/min
Re	Reynolds number	-
RWTH	Rheinisch Westfälische Technische Hochschule Aachen	-
SEM	Scanning Electron Microscope	-
Sh	Sherwood number	-
SiO_2	Silica	-
T	Temperature	^oC
TBA	Tertiary butyl alcohol	-
THF	Tetrahydrofurane	-
VLE	Vapour Liquid Equilibrium	-
VP	Vapour permeation	-
Wf	Water concentration feed	-
Wp	Water concentration permeate	-
Wr	Water concentration retentate	-

6. ACKNOWLEDGEMENT

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Appendix A Partnership

Partnership

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