Membrane Technology in the Chemical Industry. Edited by S. P. Nunes and K.-V. Peinemann
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S. P. Nunes and
K.-V. Peinemann (Eds.)

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in the Chemical Industry

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(courtesy of M. Schossig-Tiedemann).

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Preface

Membrane technology has gained a huge importance in the last 30 years, competing with long established technologies for water desalination, food processing and emerging as an unique solution in medical applications such as artificial kidney. Figuring out the fields to which membranes are already serving as important tools but also to which the membrane technology could add new solutions in the near future, the chemical industry is certainly one of the most interesting. Reason for that is the possibility of recovering valuable products as well as treating effluents and minimizing environmental problems, which are usually claimed to be caused by the chemical industry. Membranes are also now playing a special role in the field of alternative energy, as one of the fundamental parts of a fuel cell. In this sense membrane technology has a potential contribution for a green chemistry. On the other hand optimizing processes and supplying membranes for chemical applications is a large challenge for membrane scientists. In many cases a very high chemical stability is required.

The first part of the book discusses fundamental aspects of membrane processes and gives an idea of membranes, which are already available for application in the chemical industry.

The second part of this book reviews the several fields of application of the membrane technology in the chemical industry. The invited authors in part II have a long experience in the industry and are well known in the field of membrane science. They show concrete examples and discuss the advantages and eventual hindrances for membrane processes such as gas separation, pervaporation, nanofiltration and electrochemical processes in chemical applications. New possibilities for effective chemical processes in membrane reactors are presented. The future perspectives of membrane technology for the chemical industry are critically discussed in the last chapter.

Finally a few words on editing a book like this. When you have never done this, you might think it is an attractive job, collecting a number of contributions and putting your name on the front cover. This is only one part of the story, but you also make some new experiences. In the beginning everybody is exited but when the publisher's deadline is approaching you can broaden your knowledge in the field of excuses. The most common is of course “my hard disk broke down, I need two months more” but you also hear “I broke my hand and cannot continue writing” or “my computer has been stolen”. The strangest experience was that one of the originally planned contributors disappeared totally 5 weeks before the final deadline. He did not answer faxes, letters, e-mails, he even did not open the door, when we were knocking.

Now, these stories are of course not true for the actual contributors of this book. On the contrary, we express our sincere gratitude to the authors of the different chapters in part two of the book. Two of them actually stepped in four weeks before deadline and did a tremendous job.

The idea to this book came after two workshops on membrane technology in the chemical industry that we organized at GKSS. We thank Wiley-VCH for inviting us to write/edit the book and we hope to stimulate even more the incorporation of membrane technology in chemical processes in the near future. Last not least we express our thanks to the GKSS management, which gave us time and resources to edit this book.

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Part I

Membrane Materials and Membrane Preparation

S.P. Nunes and K.-V. Peinemann

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1 Introduction

Membrane technology is presently an established part of several industrial processes. Well known is its relevance in the food industry, in the manufacture of dairy products as well as in the automotive industry for the recovery of electro-painting baths. Membranes make possible the water supply for millions of people in the world and care for the survival of the unnumerable people suffering from kidney disease. The chemical industry is a growing field in the application of membranes, which, however, often requires membrane materials with exceptional stability. The first part of the book will discuss the currently available membranes for different processes, which are suitable for the chemical industry. Information on different methods of membrane preparation will be given. Different materials will be compared, taking into account physical characteristics and chemical stability.

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2 Membrane Market

The membranes and module sales in 1998 were estimated at more than US$ 4.4 billion worldwide [1], shared by different applications (Fig. 1). If equipment and total membrane systems are also considered, the estimate would be double. This amount according to data from 1996 [2], about 45 % of the sales were in the United States and 29 % in Europe and the Middle-East. The market in Asia and South America is growing fast.

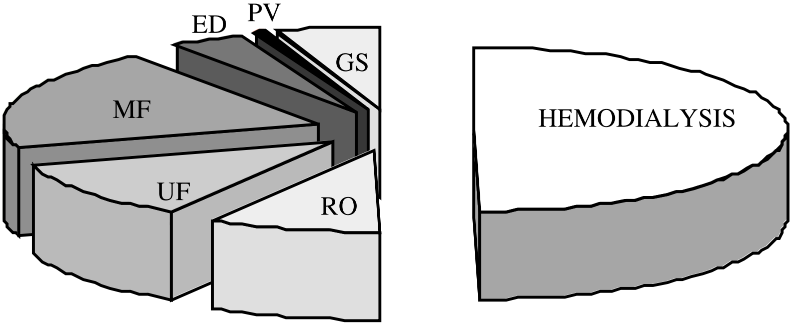

Fig. 1: Membrane and module sale for different process applications.

Hemodialysis/hemofiltration alone had sales of over US$ 2200 million in 1998. Reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) together accounted for 1.8 billion dollars in sales. About US$ 400 million membranes and modules are sold each year worldwide for use in reverse osmosis. About 50 % of the RO market is controlled by Dow/FilmTec and Hydranautics/Nitto. They are followed by Du Pont and Osmonics. Membranes are applied during sea water desalination, municipal/brackish water treatment and in the industrial sectors. The market is expected to grow at a rate of 10 %/year.

Ultrafiltration membranes and modules brought about US$ 500 million in sales in 1998 with an expected growing rate of 10 % a year. Over 58 % of the sales are in the US. In contrast to RO, the UF-market is shared by a large number of companies, but the leaders are Pall, Amicon/Millipore and Koch. One of the largest industrial sectors for ultrafiltration is still the recovery of electrocoat paints. UF-membranes are also in large scale responsible for supplying pure water for the semiconductor industry. Growing demands of ultra-high purity chemicals in this sector could also be supplied by

UF with the availability of chemical resistant membranes. Oil/water separation is now a large application for UF in industrial sectors such as metal cleaning and wool scouring and is still growing with the implementation of new environmental legislation.

Microfiltration stands for US$ 900 million worldwide sales, mostly in the US, with growing rates of 8 % a year. Main applications are the production of sterilized water for the pharmaceutical and biotechnology industry. In the semiconductor industry, MF is used to remove particles from air and produce pure water.

Gas separation (GS) is a relatively young technology and accounts for about US$ 230 million/year, but is growing fast with a rate higher than 15 % a year. For the electrically driven membrane processes the sales in 1998 were around US$ 180 million. For pervaporation (PV) in 1996 the market was about US$ 26 million, with a growing rate of 20 %.

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3 Membrane Preparation

Different methods of polymer membrane preparation have been covered in several reviews [4–7]. Membranes can be classified, according to their morphology as shown in Fig. 2.

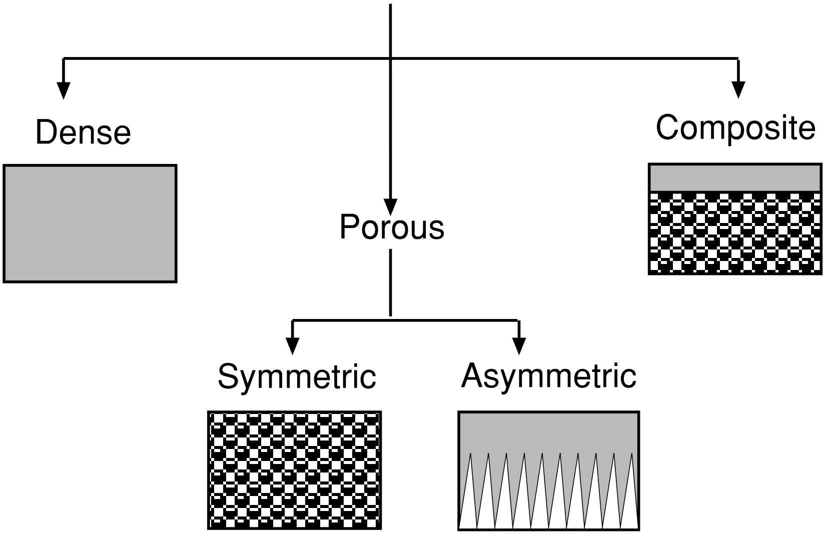

Fig. 2: Membrane classification according to the morphology

Dense homogeneous polymer membranes are usually prepared (i) from solution by solvent evaporation only or (ii) by extrusion of the melted polymer. However dense homogeneous membranes only have a practical meaning when made of highly permeable polymers such as silicone. Usually the permeant flow across the membrane is quite low, since a minimal thickness is required to give the membrane mechanical stability. Most of the presently available membranes are porous or consist of a dense top layer on a porous structure. The preparation of membrane structures with controlled pore size involves several techniques with relatively simple principles, but which are quite tricky.

Commercial membranes were already produced in Germany by Sartorius in the early 20's. However they had only a limited application on a laboratory scale. The breakthrough of the membrane technology came first in the 60's with the development of the asymmetric porous membranes by Loeb and Sourirajan [8]. The asymmetric membranes combine high permeant flow, provided by a very thin selective top layer and a reasonable mechanical stability, resulting from the underlying porous structure. An asymmetric structure characterizes most of the presently commercially available membranes, which are now produced from a wide variety of polymers. By far the most common method used in generation of asymmetric structures in membranes is the "phase inversion" process. Other methods used to form pores in membranes will be discussed in the following sections. Particularly in the case of microfiltration, several techniques other than phase inversion are currently applied in the industry.

Phase inversion

The phase inversion process consists of the induction of phase separation in a previously homogeneous polymer solution either by temperature change, by immersing the solution in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process).

In the thermal process [9, 10], a low molecular weight component usually acts as a solvent at high temperature and as a non-solvent at low temperature. It is then removed after formation of the porous structure. Although the thermal process can be applied to a wide range of polymers, it is especially interesting for those with poor solubility, such as polypropylene, which can be hardly manufactured into a porous membrane by other phase inversion processes. An isotropic microporous structure is usually formed.

The isothermal phase inversion is commercially more widespread. Usually the polymer solution is immersed in a non-solvent bath (wet process) and a solvent-non-solvent exchange leads to phase separation. The polymer rich phase forms the porous matrix, while the polymer poor phase gives rise to the pores. The morphology is usually asymmetric, with a selective skin on the surface, as shown in Fig. 3.

The pore structure is generated by phase separation. Phase separation in this case is mainly a liquid-liquid demixing process, although solid-liquid demixing may also play an additional role in systems containing a crystallizable polymer, such as cellulose acetate and poly (vinylidene fluoride). After immersion in a non-solvent bath, the solvent-non-solvent exchange brings the initially thermodynamically stable system into a condition, for which the minimum Gibbs free energy is attained by separating into two coexisting phases. The predominant mechanism of phase inversion leading to pore formation and the thermodynamics involved are the subject of a fruitful and sometimes controversial discussion in the literature [11–26], as well as the most probable paths in the phase diagram.

A simplified diagram is shown Fig. 4.

Basically the mechanism of phase separation depends on the crossing point into the unstable region. If the solvent-non-solvent exchange brings the system first to a metastable condition (Path A), the nucleation and growth mechanism (NG) is favored. A

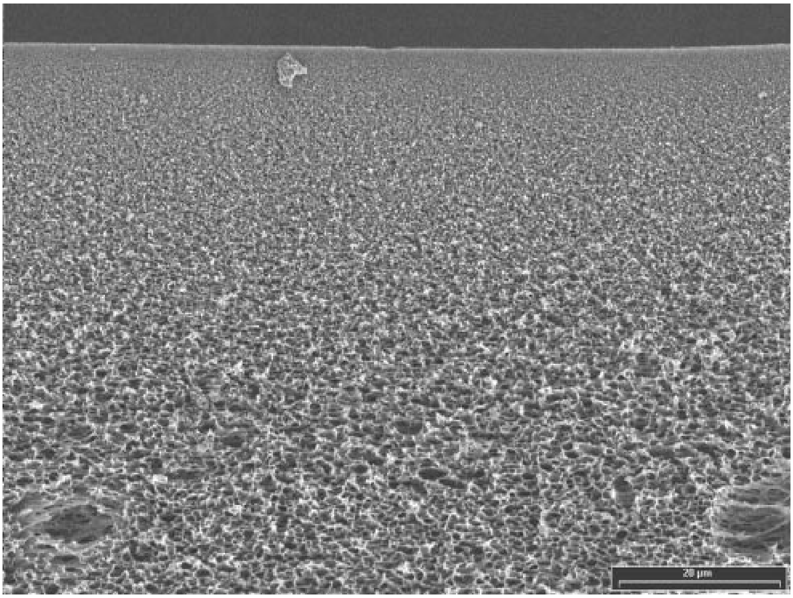

Fig. 3: Asymmetric porous membrane.

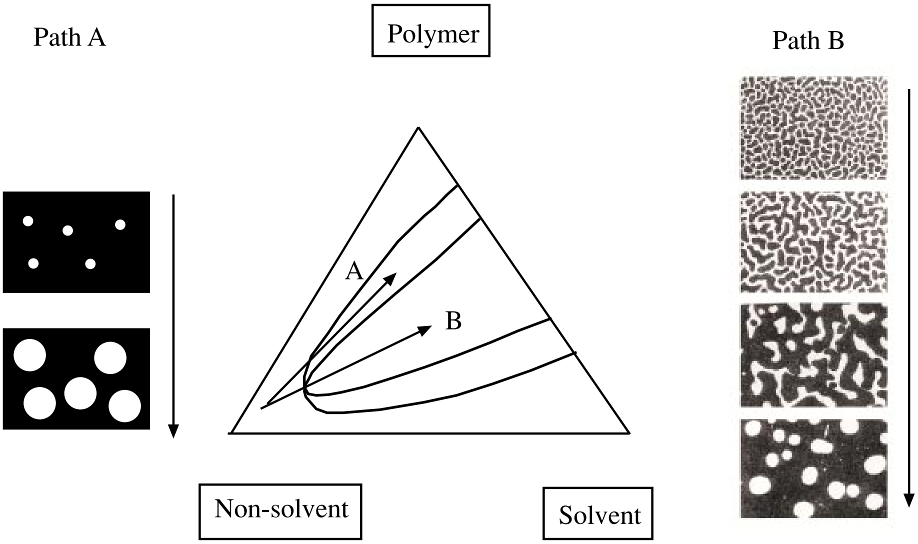

Fig. 4: Mechanism of phase separation during membrane formation.

dispersed phase consisting of droplets of a polymer poor solution is formed in a concentrated matrix. If no additional non-solvent influx or temperature change in the system were induced, the composition inside the nuclei would be, from the beginning, that expected at the equilibrium and would, practically, not change with time. Only the size of the droplets increases with time. If the demixing path crosses the critical point, going directly into the unstable region (Path B), the spinodal decomposition (SD) predominates. A concentration fluctuation appears in the initially homogeneous system and progresses with increasing amplitude, leading to a separation in two co-continuous phases. Here again the polymer poor phase will form the pores. The initial steps of phase separation, either by NG and SD can be relatively well described according to theories of phase separation. However, at later stages, both NG and SD usually progress to a phase coalescence and the final structure can only be predicted with difficulty.

At least as important as the starting mechanism of phase separation is the point where the developing structure is fixed. Parallel to demixing, as the concentration of the polymer solution changes, by solvent-non-solvent exchange, the mobility of the system decreases. Reasons for that may vary from physically unfavorable polymer-solvent (or non-solvent) interaction, leading to stronger polymer-polymer contacts, to vitrification of the polymer concentrated phase, as the solvent concentration decreases, and also in some cases partial crystallization. If the system gels and solidifies directly after the first steps of phase separation (for instance at t_2), the membrane will have a fine pore structure, which keeps the original characteristics given by the initial demixing mechanism. If NG demixing stops during the initial stages, a morphology of closed cells would be favored. At later NG stages, the nuclei would grow and touch each other forming interconnected pores. The SD demixing would favor the formation of an interconnected pore structure from the beginning.

An asymmetric structure is usually formed across the membrane since the solvent-non-solvent exchange may lead to different starting conditions for phase separation at layers far from the surface. Besides the NG and SD demixing, other factors influence the morphology. The whole membrane structure usually can be classified as sponge-like or finger-like.

Finger-like cavities are formed in many cases, as the non-solvent enters the polymer solution. This macrovoid structure may contribute to a lack of mechanical stability in membranes to be used at high pressures. A combination of factors is responsible for the formation of macrovoids and this topic has been well reviewed in the literature [27, 28]. For practical purposes, the predominance of a sponge-like or a macrovoid structure can be induced in different ways. Basically, the sponge-like structure is favored by

i) increasing the polymer concentration of the casting solution
ii) increasing the viscosity of the casting solution by adding a crosslinking agent
iii) changing the solvent
iv) adding solvent to the non-solvent bath

The growth of a polymer poor phase by SD or NG is an isotropical processes, which take place as soon as the solvent-non-solvent contents supply the thermodynamic condition for demixing. To understand the macrovoid formation, a quite interesting explanation was provided by Koros [27] as depicted in Fig. 5. For that, the coupling of the (NG or SD) demixing processes with the rapidly moving front of non-solvent must be considered. If the non-solvent diffusion rate into the polymer poor phase being formed exceeds the rate of outward solvent diffusion, the macrovoid formation is favored. The diffusivity of water is usually expected to be one-to-two orders of magnitude higher than the diffusivity of bulkier organic solvents. The main driving force for the non-solvent (usually water) influx is the locally generated osmotic pressure. This could be hypothetically approximately 100 bar with a difference of only 5 mol % non solvent concentration between the initial nucleus and the approaching front. As water moves into a polymer poor nucleus, its wall is deformed, expanding in the form of a tear. If the walls are fragile, the nucleus may rupt giving rise to macrovoids with unskinned walls. If the walls are stronger, as in the case of nuclei growing in a matrix with higher polymer concentration, the deformation can be restrained or even totally inhibited, giving rise to a macrovoid free structure.

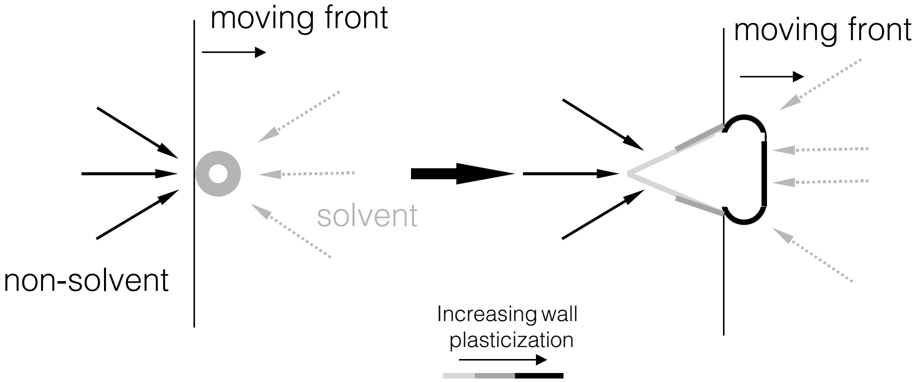

Fig. 5: Non-isotropic nucleus growth during macrovoid formation in membrane.

Increasing the polymer concentration of the casting solution to suppress macrovoids has been well registered in the literature for a wide spectrum of polymers such as cellulose acetate [28], aromatic polyamide [29], and polyetherimide [30]. Other factors such as the addition of crosslinking agents which can improve the strength of the growing nucleus wall also contribute to a macrovoid free structure. An example is the addition of amines to polyetherimide casting solutions [31].

Another way to suppress the macrovoid formation is to reduce the osmotic pressure between the non-solvent moving front and the polymer poor phase inside the nuclei. This can be achieved by adding non-solvent to the casting solution or adding solvent to the non-solvent bath. An example is the addition of dioxane to an aqueous coagulation bath for a CA dioxane solution [28].

Changing the solvent may act in different ways. Solvents with higher diffusivity across the nucleus walls would be able to leave the nucleus faster, while the non-solvent is added in, which does not favour macrovoid formation. But even more effective in suppressing the macrovoid formation are solvents which increase the solution viscosity or even promote a fast gelation, making the nucleus wall stronger and resistant to deformation. Some examples of solvent influence on membrane morphology are to be found in the literature for polyetherimide [30] (Fig. 6) and cellulose acetate [32].

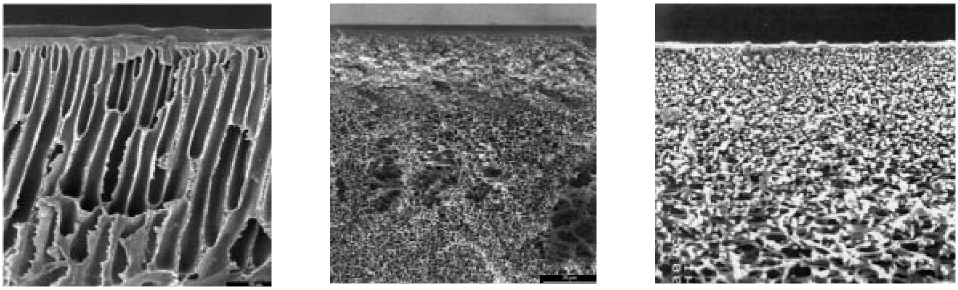

Fig. 6: Polyetherimide (PEI) membranes prepared from different casting solutions: (left) 17.5 wt % PEI in dimethylacetamide; (middle) 17.5 wt % PEI in 5.5 wt % tetraethoxysilane and 77 wt % dimethylacetamide; (right) 15.5 wt % PEI in 28 wt % THF and 56 wt % g-butyro lactone.

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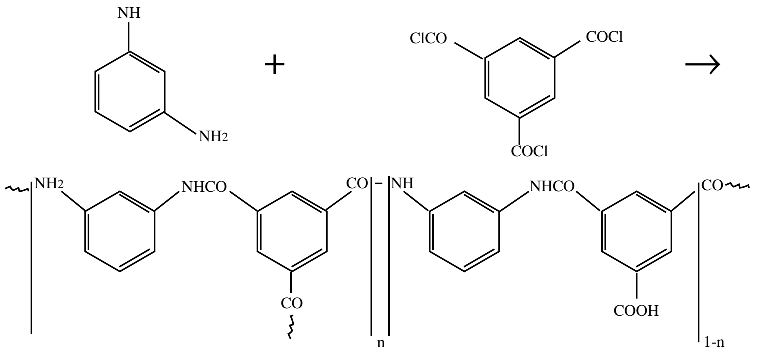
4 Presently Available Membranes for Liquid Separation

4.1 Membranes for reverse osmosis

The most common membrane materials for reverse osmosis membranes are cellulose acetate, polyamide and the "thin film composites", prepared by interfacial polymerization on the surface of a porous support. A review of composite membranes was published by Petersen [33]. Cellulose acetate (CA) was one of the first membrane materials, and it is still being successfully used, especially in water treatment (in spiral wound modules). They usually allow quite high water flows with low salt solubility. One advantage, when compared to the polyamide based membranes, is its chlorine tolerance. Also because of the neutral surface, cellulose acetate membranes usually exhibit a more stable performance than polyamide membranes in applications where the feed waters has a high fouling potential, such as in municipal effluents and surface water supplies. However, CA membranes are drastically less stable in organic solvents than polyamide. The recommended pH range is between 3 and 7, they are less resistant to biological attack and the recommended temperature is lower than 50°C. The susceptibility to hydrolysis increases with temperature and is an inverse function of the degree of acetylation. Aromatic polyamides have a much higher solvent resistance and may be used in a wider pH range (pH 4–11). The main application is the treatment of brackish water and seawater. They can be produced in very thin hollow fibers with large surface area/volume. The membrane top layer is however quite thick (>0.2 µm), which leads to relatively low water flows. The main disadvantage is the very low chlorine tolerance.

Integral asymmetric membranes have a relatively low manufacturing cost. CA in particular, dominates a significant part of the membrane market for water treatment due to its low cost. However the possibility of expanding the application of reverse osmosis in separations which demand membranes with higher performance came only with the advent of the thin film composite (TFC) membranes. They consist of an ultrathin layer, usually of polyamide or polyetherurea, which is polymerized in situ and crosslinked on an asymmetric porous support, usually polysulfone. Since the dense selective layer is very thin, the membranes can operate at higher flux and lower pressure. The chemical stability is very good, although the chlorine tolerance is low. They are not biodegradable and can operate in a pH range of between 2 and 11. The membrane preparation consists of immersing the porous support in an aqueous solution containing a water-soluble monomer. After that the support is immersed in a solution of the second monomer in a non-polar solvent. Both monomers are only allowed to react at the interface between organic and aqueous solution, forming a thin polymer layer at the surface of the porous support. As soon as the polymer layer is formed it acts as a barrier for the monomer transport and avoids the continuity of the polycondensation. On the other hand, any defect on the polymer layer is immediately repaired, since monomer transport and polycondensation is allowed at that point. One of the most successful TFC membranes is the FT-30, developed by Cadotte [34] in the North Star Laboratories and presently commercialized by Dow. The reaction involved in the preparation of the FT-30 is as follows:



The polyamide layer is formed on an asymmetric microporous polysulfone support cast on a polyester support web. The polyester web gives the major structural support and the polysulfone support with small surface pores with diameter of ca. 15 nm is the proper substrate for the formation of a 0.2 µm polyamide top layer (Fig. 7). The FT-30 has been optimized for different applications, being commercialized [35] as FILMTEC TW-30 (for municipal tapwater), BW-30 (for brackish water) and SW-30 (for sea water conversion to potable water). Salt rejections higher than 99.5 % can be obtained with fluxes of 0.6 m^3/m^2 day or rejection. With 0.2 % salt feed solution, membranes work at

Tab. 1: Rejection of different solutes by FT30

Solute	**Molecular weight (g/mol)**	**Rejection (%)**
Sodium chloride	58	99
Calcium chloride	111	99
Magnesium sulfate	120	>99
Copper sulfate	160	>99
Formaldehyde	30	35
Methanol	32	25
Ethanol	46	70
Isopropanol	60	90
Urea	60	70
Lactic acid (pH2)	90	94
Lactic acid (pH 5)	90	99
Sucrose	342	99

2000 ppm solute, 1.6 MPa, 25 °C, pH7 (unless otherwise noted)

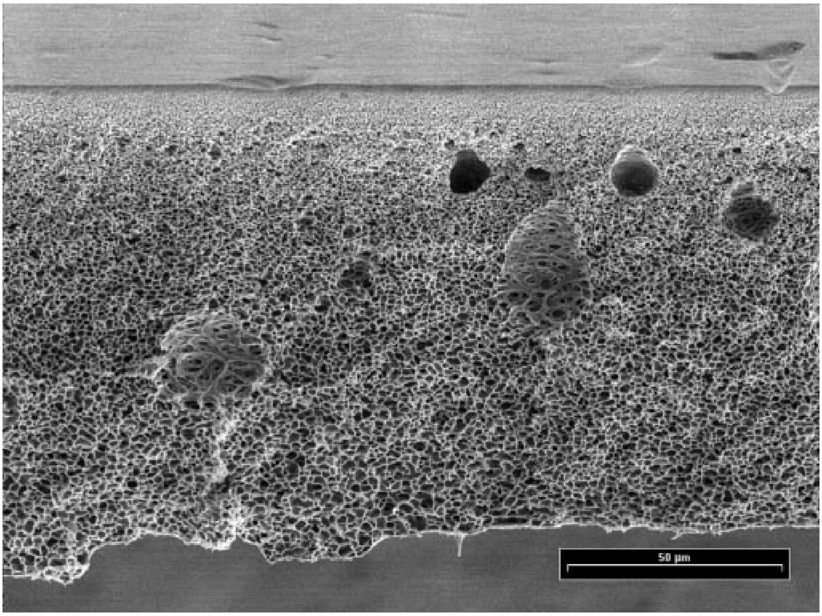


Fig. 7: FILMTEC® FT-30.

1.6 MPa with rejections above 98 % and fluxes of 1 m^3/m^2 day. This represents a reduction up to 50 % in operating pressure for water treatment in comparison to commercial cellulose acetate membranes. The rejection of other solutes by FT 30 is shown in Tab. 1. The maximum operating pressure of the FT 30 is about 7 MPa with free chlorine tolerance < 0.1 ppm.

Tab. 2: Characteristics of NITTO DENKO RO membranes.

NITTO DENKO Energy Saving ES 10 and ES 15	
Max. Feed Temperature:	40°C
pH:	2–10
Residual chlorine:	zero
ES 10 operating conditions (2 inch spiral wound element):	
Max. inlet pressure:	4.2 MPa
Standard inlet pressure:	0.75 MPa
NaCl rejection:	99.5 % (1500 ppm feed at 7.5 bar, 25°C, pH 6.5)
Average water flux:	1.7 m^3/m^2 day
ES 15 operating conditions (8 inch spiral wound element):	
Max. operating pressure:	2 MPa
NaCl rejection:	99.5 % (1500 ppm feed at 7.5 bar, 25°C, pH 7)
Average water flux:	37 m^3/m^2 day

Another very successful development for reverse osmosis is the energy saving membrane series produced by Nitto Denko (Tab. 2). The membrane filtrating layer is also an aromatic polyamide. Due to its irregular surface, the actual membrane area available for the permeation is much larger than it would be in the case of a smooth surface on the same porous support. High fluxes are therefore obtained.

4.2 Membranes for nanofiltration

While reverse osmosis and ultrafiltration were being established in several applications, there was a lack of available membranes with cut offs between 400 and 4,000 g/mol. An increasing interest in NF membranes developed in the last decade. One of the main applications is water softening. The following membranes are recommended for use in water softening systems: UOP Fluid Systems modules 8231-LP (cellulose acetate blend) and 8921-UP (TFCS polyamide), FILMTEC NF 70 and NF 40, Toray modules SCL-100 (modified cellulose acetate) and SU 600 (composite polyamide), Nitto Denko NTR-729 HF, Desalination Systems Desal-5 and DuPont SM15 [33, 36].

However the improvement of solvent stability of available NF-membranes opens a wide range of potential applications in the chemical and pharmaceutical industry.

FILMTEC/Dow has commercialized the NF55, NF70 and NF90 (water flow of NF55 > NF70 > NF90) membranes, which work in the range of nanofiltration, being able to reject at least 95 % magnesium sulfate. The top layer in this case is a fully aromatic crosslinked polyamide. The exact composition is not known. The chlorine tolerance is lower than 0.1 ppm and the pH range in operation is 3–9. One procedure to prepare nanofiltration membranes is the interfacial polymerization between a piperazine or an amine substituted piperidine or cyclohexane and a polyfunctional acyl halide as described in US Pat 4769148 and 4859384 [37, 38]. Another way to obtain nanofiltration membranes is the modification of reverse osmosis membrane, as proposed by Cadotte [39]. The process involves contacting a crosslinked polyamide selective layer with a strong mineral acid such as phosphoric acid at 100–150 °C, which is then followed by a treatment with a "rejection enhancing agent" such as tannic acid or water-soluble polymers to selectively plug microscopic leaks and defects. Another procedure [40] to open polyamide RO-membranes consists of contacting the membrane with ions to form a membrane ion complex, treating the membrane-ion complex with an aqueous solution of an alkali metal permanganate to form manganese dioxide crystals in the membrane and finally dissolving the crystals. In another procedure a reverse osmosis membrane is treated with triethanolamine to open the pores [41]. RO cellulose acetate membranes can be opened by hydrolysis at very high and very low pH. However it is difficult to control this process.

Nanofiltration membranes can also be obtained by coating ultrafiltration membranes with different polymer solutions. Membranes with cut offs between 800 and 4500 g/mol and water permeabilities of up to 10 l/h m^2 bar could be obtained by coating PVDF membranes with polyether-block-polyamide copolymers [42]. A lower cut off was obtained by forming a polyamide network dispersed in the blockcopolymer layer by reacting a polyether diamine and trimesoyl chloride [43]. Coatings of hydroxyalkyl derivatives of cellulose are used to prepare solvent resistant membranes [44].

Also in the range of nanofiltration the ESPA membrane, made of anionic aromatic polyamide, has been commercialized by Hydranautics [45] and the D- and H-Series membranes are produced by Desal/Osmonics [46]. The D-Series, which are thin-film nanofiltration membranes, have a molecular weight cut off of 150-300 g/mol for uncharged organic molecules and can operate at pH values of less than 1. They have been applied, for instance, by printed circuit board manufacturers to recover soluble copper from acid rinse streams. Copper sulfate from acid rinse streams of a copper refinery has also been successfully recovered with D-Series membranes. Another successful case was the recovery of ammonium sulfate from ground water contaminated by a nickel refinery.

In a recent report [47] the membranes Desal-5, from Osmonics, NF 45, from Dow, and PVD-1 from Hydranautics, have been compared according to their performance in the separation of metal sulfates and nitrates from their acids. The membrane characteristics, as provided by the manufacturer and the retention of different ions are shown in Tab. 3. During the tests with solutions containing multivalent salts, Desal-5 had the lowest flux and NF 45 the highest.

Tab. 3 Characteristics of some NF membranes in comparable conditions.

Membrane	Permeability	Cut off	Retention (%)					
	(m^3/m^2 day MPa)	(g/mol)	Fe^{3+}	Cr^{3+}	Ni^{2+}	SO_4^{2-}	NO^{3-}	F^-
Desal-5	1.3	150-300	89.8	90.1	90.4	64.8	36.8	61.3
PVD-1	0.8	180	96.0	96.4	96.4	71.4	24.8	69.6
NF 45	1.2	–	99.0	99.6	99.7	56.9	25.0	71.0

Cations of higher valency had a higher retention, especially in the case of NF 45, which might be positively charged.

4.3 Membranes for ultrafiltration

Table 4 lists some commercially available membranes for ultrafiltration. The development of UF membranes form different polymer materials is commented below.

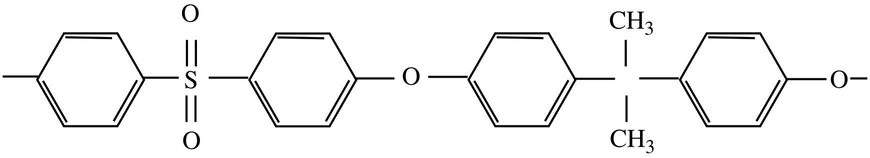
Tab. 4: Some commercially available membranes for ultrafiltration.

Trade name	**Membrane material**	**Cut off (g/mol)**	**pH range**	**Max. operating temperature (°C)**	**Protein adsorption (mg/cm²)**
Millipore					
PL Ultrafilter	Cellulose	1,000–300,000	2–13	35–50	1
PT Ultrafilter	Polysulfone	10,000–300,000	1–14	50	<100
PALL Gelman					
Nova	Polyethersulfone	1,000–1,000,000	1–14	40	58
Omega(TM)	Low protein-binding polyethersulfone	1,000–1,000,000			2
Desal					
P-Series	Polysulfone	10,000	2–10	50	
G-Series	”Thin-film (TFM”)”	1,000–10,000	2–11		

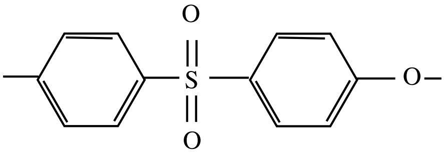
Polysulfone and polyethersulfone

UF-membranes are usually prepared by phase inversion. The most widely used polymer for the preparation of UF-membranes is polysulfone (PSU) or polyethersulfone (PES).

Polysulfone



Poly (ether sulfone)



The first developments of PSU membranes appeared in the 60’s as an alternative to cellulosic membranes. Since then several procedures have been described in the literature for PSU membranes [48, 49], in many cases using the high molecular weight polysulfone Udel P-3500 commercialized by Amoco. A great advantage when compared to cellulose acetate is its resistance in extreme pH conditions, as well as its thermal stability. PSU has a Tg of 195 °C and PES even higher, at 230 °C. Both PSU and PES are soluble in chloroform and dimethylformamide, and are easily applied in conventional phase inversion processes. This high solubility is also the main drawback of PSU as a membrane material, eliminating the use of polysulfone-supported membranes in the processing of solvent-based feed solutions. It is also a problem coating the PSU support with polymers, which are only soluble in organic solvents. Another disadvantage of PSU and PES membranes is their hydrophobic character, which prevents spontaneous wetting with aqueous media. Consequently, the membrane must be prevented from drying completely or the membrane must be treated with a hydrophobic agent, glycerin, for example, before drying. Another serious disadvantage of hydrophobic materials consists in the fact that they often possess a powerful nonspecific adsorption capacity.This phenomenon, known as fouling, leads to a rapid deterioration of the membrane permeability. Suggestions for hydrophilic membranes have already been proposed that do not suffer from these disadvantages. Several procedures have been proposed to make membrane surface more hydrophilic and they will be discussed later. One effective way to make polysulfone membranes more hydrophilic is to prepare the membranes from a mixture of sulfonated and non-sulfonated polysulfone [50, 51]. The sulfonation may be controlled to limit the water solubility of the resulting polymer. Insolubilization can also be achieved by crosslinking with additives such as polyols or polyphenols. Sulfonation has been a successful alternative to the incorporation of other hydrophilic polymers, which are soluble in water. Preparation of membranes from polymer blends with hydrophilic polymers has been well described in the literature [49, 52]. Polyvinylpyrrolidone is one of the commonly applied polymers for this purpose [18]. Another common additive is poly(ethylene glycol) [53]. However hydrophilization of membranes by using large quantities of water-soluble polymers has the disadvantage that the hydrophilic nature of the membrane constantly decreases when they are used in aqueous media, since the water-soluble polymer is washed out. Although not completely described, sulfonated polysulfone probably coats polysulfone supports in the G-series membranes commercialized by Desal. Sulfonated polysulfone seems to also play an important role in nanofiltration and reverse osmosis membranes commercialized by Desal. According to Petersen [33] the Desal-5 membrane appears to consist of three layers: a microporous polysulfone, a sulfonated overlay and a top highly ultrathin layer based on polypiperazineamide.

Poly (vinylidene fluoride)

$$–(CF_2 – CH_2) –$$

PVDF

Poly (vinylidene fluoride) (PVDF) is quite interesting in the manufacture of UF-membranes due to its chemical resistance. PVDF is resistant to most inorganic and orga-

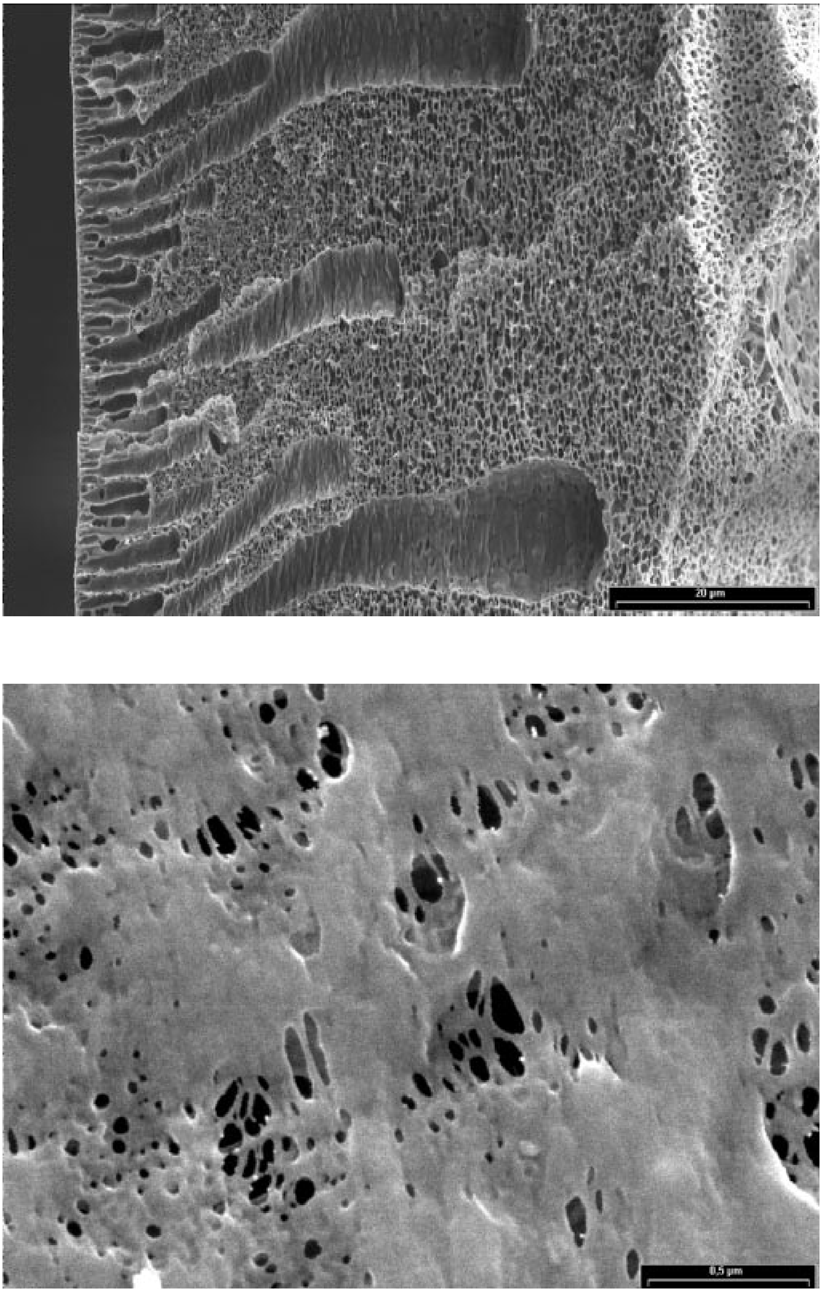
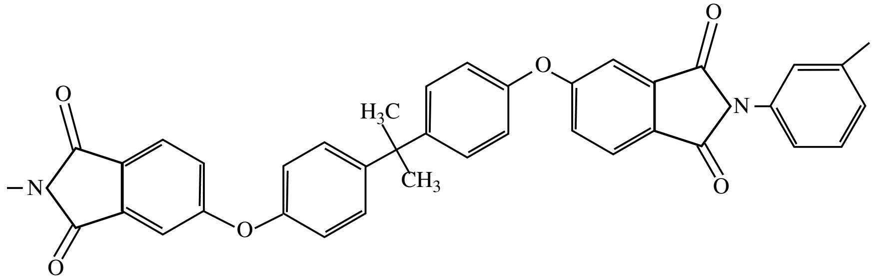


Fig. 8: Poly(vinylidene fluoride) membrane: (top) cross-section and (bottom) surface.

nic acids and can be used in a wide pH range. It is also stable in aromatic hydrocarbons, alcohols, tetrahydrofurane and halogenated solvents. Furthermore it is resistant to oxidizing environments including ozone, which is used in water sterilization. PVDF is semi-crystalline with a very low Tg (–40°C), which makes it quite flexible and suitable for membrane application in temperatures ranging between –50 and 140 °C, just prior to its melting temperature. Although stable in most of organic solvents, PVDF is soluble in dimethyl formamide, dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP) and dimethylsulfoxide, making membrane preparation by phase inversion possible. In an early patent [54] on PVDF membranes, solutions containing about 20 % PVDF in DMAc were cast and immersed in a methanol bath. Later [55] a preparation was described using a casting solution in DMAc, containing also ca. 17 % isopropanol and using an immersion bath with about 40 % water, 50 % DMAc and 7 % isopropanol. Membranes are also prepared from solutions in NMP containing litium chloride and an immersion bath of methanol. US Pat 4203848 [56] describes the preparation of PVDF membranes by dissolving the polymer in boiling acetone and immersing it in a cold water/acetone bath. Another interesting solvent is triethyl phosphate (TEP) [57], a basic solvent, which complexes with the acidic PVDF [3]. The morphology of a PVDF membrane obtained from a solution in DMAC is shown in Fig. 8. Like polysulfone, PVDF is highly hydrophobic and many attempts to make them more hydrophilic have been described in the literature. One procedure is the chemical treatment with a strongly alkaline solution either in the presence of an oxidizing agent [58] or with a polymerization initiator and monomers such as acrylic acid [59]. The membrane surfaces have also been grafted or coated with polyacrylamide, poly(acrylic acid) [60, 61] poly (vinyl alcohol) and cellulose derivatives [62]. Another possibility for improving the membrane properties is the use of polymer blends. Blends of PVDF/ PVP [63, 64], PVDF/poly (ethylene glycol) (PEG) [65], PVDF/sulfonated polystyren [66], PVDF/poly (vinyl acetate) [67] and PVDF/poly (methyl methacrylate) [68] have been used in the preparation of microporous membranes.

Polyetherimide



PEI

Polyetherimide (PEI) is an amorphous polymer with Tg near 200 °C. It can be used at temperatures higher than PVDF and it is known for its superior strength. The chemical stability, although much higher than cellulosic polymers, is lower than that of PVDF. PEI can not be used in contact with chloroform and dichloromethane. It is also attacked by tetrahydrofurane. The stability at high pH is poorer than that of PVDF, PSU or PAN. The preparation of membranes from PEI solutions leads to a large variety of porous asymmetric structures, which can be controlled by changing the composition of the solvent mixture. The commercial polymer usually chosen is Ultem® 1000, manufactured by General Electric. Integral asymmetric membranes are quite successful in gas separation [69], particularly in the case of helium recovery. More open asymmetric PEI supports have been used for ultrafiltration or as support for composite membranes. Usually a porosity higher than that of PVDF membranes is obtained with smaller average pore size as shown in Fig. 9. Porous PEI membranes with a dense and thin top layer for for gas separation were initially prepared from a solution in a mixture of dichloromethane, 1,1,2-trichloroethane, xylene and acetic acid and coagulated in acetone [69]. Another solvent mixture later allowed the preparation of PEI membranes for gas separation coagulated in water. For that a mixture of tetrahydrofurane (THF) and gamma-butyrolactone (GBL) was used. Both THF and GBL are non-solvents for PEI, but due to an effect of cosolvency a stable casting solution is obtained. Membranes with very thin top layers are particularly formed with higher GBL contents. The addition of volatile non-solvents such as butanol to the casting solution lead to the formation of even thinner top layers. After coagulation in water a sponge-like structure is obtained. The preparation of hollow fibers from PEI solutions in a mixture of NMP and GBL or DMAc and GBL is described by Kneifel and Peinemann [30]. Here the addition of GBL, a non-solvent slightly increases the solution viscosity and favors a sponge-like structure without finger-like cavities.

Blends of PEI with other polymers are also reported to improve membrane characteristics [31]. Blends of PEI and poly (ether sulfonamide) were obtained as an attempt to improve the membrane hydrophilicity. In order to make both polymers compatible, 1,3-diamino propanol (DAP) was added to the polymer solution. DAP reacts with PEI and increases the solution viscosity. As a result, besides the compatibilization effect, the addition of DAP induces a sponge-like structure, eliminating the finger-like cavities which are usually observed in membranes obtained from PEI or PESA solutions in dimethyl acetamide. PEI is successfully used as a porous support for composite membranes. However, in order to improve their resistance to compactation at extreme conditions of high pressure and hydrocarbon atmosphere, an inorganic polymer was generated in the casting solution by hydrolysis of alkoxy silanes and incorporated in the membrane structure [70]. Here again compatibility was necessary and was achieved with the introduction of amino silanes. Also for the preparation of asymmetric porous membranes a blend of PEI polyimide with phenylindane groups (Matrimid) was reported with the purpose of improving the PEI gas permeation in hollow fibers [71].

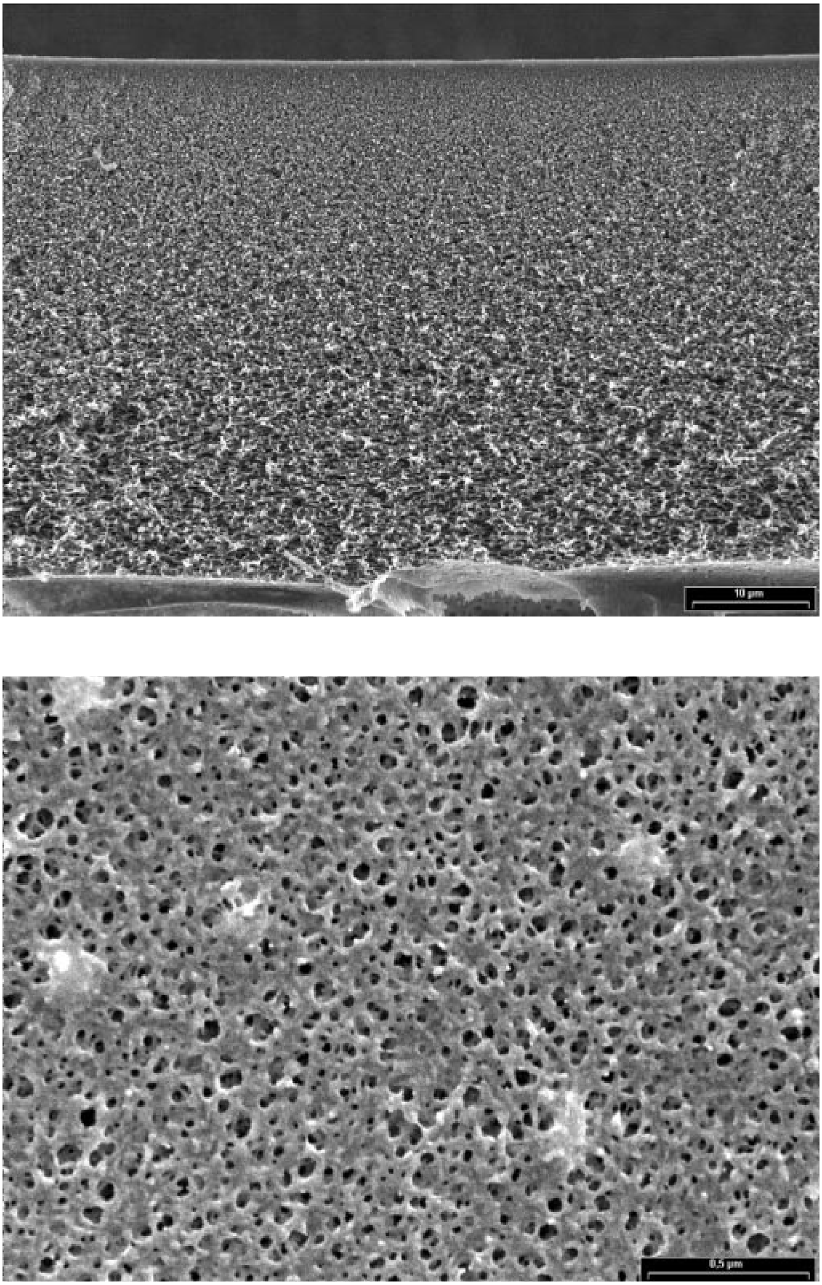
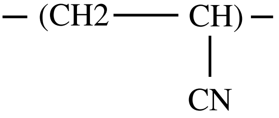


Fig. 9: Poly(etherimide) membrane: (top) cross-section and (bottom) surface.

Polyacrylonitrile

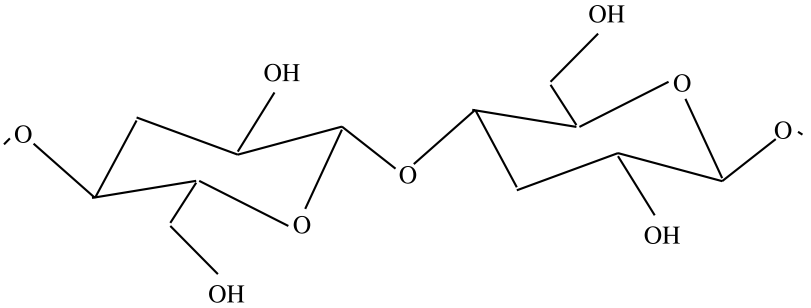


$$-(\mathrm{CH2}-\underset{\mathrm{CN}}{\underset{|}{\mathrm{CH}}})-$$

PAN

Polyacrylonitrile (PAN) has been used in the preparation of UF-membranes for a long time [72, 73] due to its superior resistance to hydrolysis and oxidation. PAN is highly crystalline and relatively hydrophilic and is usually copolymerized with more hydrophilic monomers to improve processability and to make it less brittle. Hollow fibers can be prepared from PAN dissolved in nitric acid [74]. Preparation of PAN membranes by phase inversion from solutions in DMAC, DMF or NMP is also possible. An example is shown in Fig. 10. A Sumitomo patent [75] discloses the preparation of membranes from copolymers containing 89 % acrylonitrile and 11 % ethyl acrylate dissolved in DMF and formamide and coagulated in water. A microporous membrane is obtained. In order to make the membranes suitable for reverse osmosis, they were submitted to a plasma treatment in the presence of 4-vinyl pyridine.

Cellulose



Cellulose UF-membranes are used in applications where low fouling characteristics are required. Cellulose has a very regular structure and is able to form strong intermolecular hydrogen-bonds between the several hydroxy groups. As a result, cellulose is practically insoluble in almost all solvents. The only exceptions are dilute solutions in DMAc or NMP with addition of lithium chloride. Cellulose membranes are prepared by methods which basically involve precipitation from a solution of chemically modified native cellulose (from cotton linters, etc). Until some years ago the three main methods were celluphane, cuprophane and cuenophane. Celluphane membranes are prepared by a viscose process, in which cellulose is regenerated from a cellulose xanthate solution, as described in the US Pat 981368 and 991267 [76, 77]. Cuprophane membranes are prepared in a similar way, regenerating cellulose from its soluble cop-

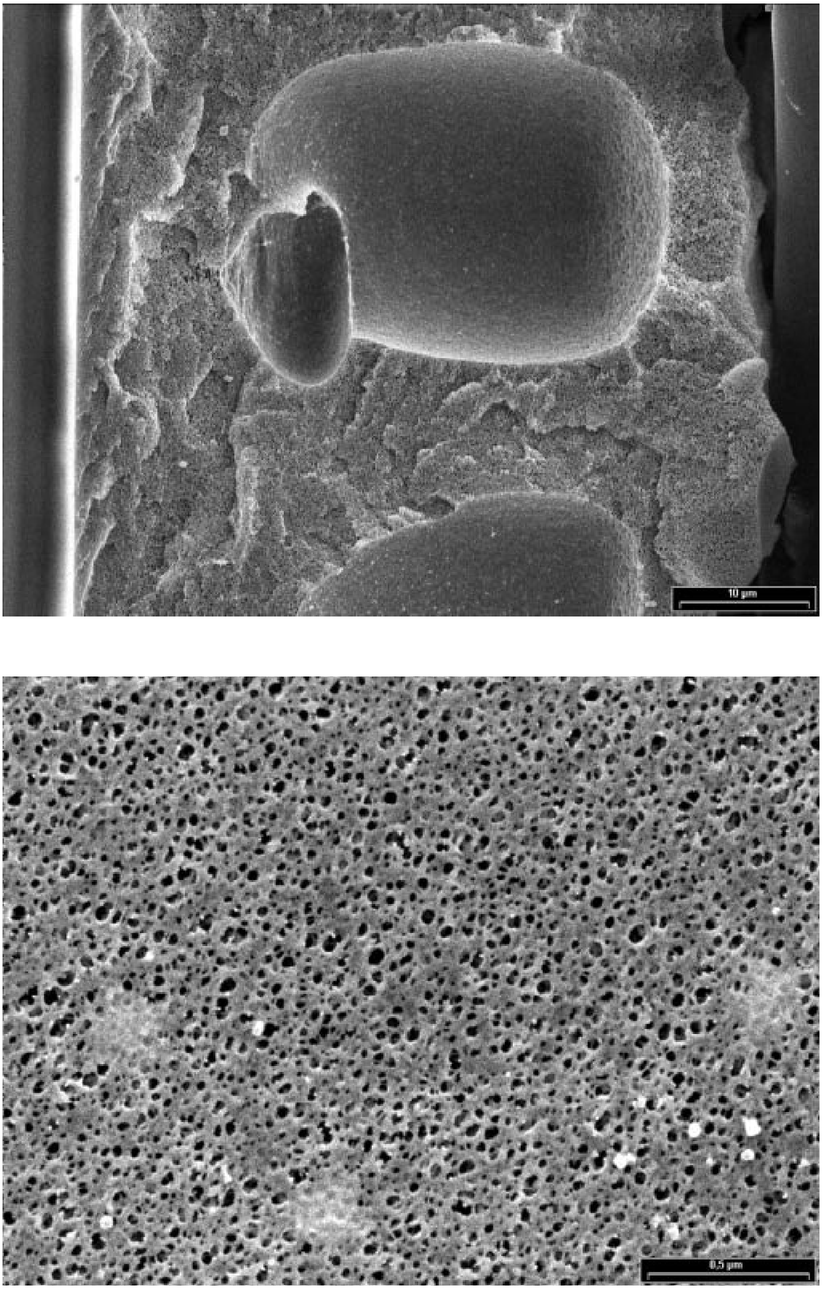


Fig. 10: Poly(acrylo nitrile) membrane: (top) cross-section and (bottom) surface.

per complex formed by reacting with ammoniacal copper sulphate, as described in US Pat 2067522 [78]. To obtain cuenophane membranes, cellulose is regenerated after dissolving it in cupriethylen diamine. For regeneration of cellulose from solution, a coagulation in strong alkali solutions is usually required. Today most of the cellulose membranes are prepared by hydrolysis of asymmetric cellulose acetate membranes [79] also in strong alkali solutions. An alternative method for the preparation of cellulose membranes has been recently proposed; acid hydrolysis of trimethyl silyl cellulose [80].

4.4 Solvent resistant membranes for nano- and ultrafiltration

A reason for the restrained application of membrane technology in the chemical industry, as compared to other fields, is the availability of well established chemical resistant membranes, which could work in harsh process conditions, eventually at extreme pH conditions or in processes with organic solvents. Although several examples have been described in the patent literature in the last decade and some are commercialized, reasonably low costs associated with a well documented long term application are usually required to make them commercially attractive and lower the risks of substituting conventional separation processes. The development of solvent resistant membranes is a relevant research topic in the leading membrane companies.

Some solvent stable membranes are discussed here and resumed in Tab. 5. Membrane Products Kiryat Weizmann Ltd developed the SelRO® nanofiltration membranes with excellent solvent resistance and are now commercialized by Koch Membrane Systems. The MPS-44, 50 and 60 are [81] claimed to have an excellent stability in alkanes, alcohols, acetates, ketones and aprotic solvents. The MPS 44 is a hydrophilic mem-

Tab. 5.: SelRO® Nanofiltration Membranes.

Membrane	**Cut off (g/mol)**	**pH range**	**Stability in organic solvents**	**Maximum temperature (°C)**
MPS-44 hydrophilic	250	2–10	excellent	40
MPS-50 hydrophobic	700	4–10	excellent	40
MPS-60 hydrophobic	400	2–10	excellent	40

brane suitable, for instance, for separation processes in solvent mixtures containing water and organics. Solutes with molecular weights ≥ 250 g/ml can then be separated or concentrated, while the composition of the solvent mixture does not change through the membrane. The hydrophilic MPS 50 and MPS 60 are nanofiltration membranes for use in a pure organic medium. Some applications include the recovery of antibiotics and pepitides from organic solvents, recovery of catalysts from organic medium and recovery of hydrocarbons from cleaning processes.

Although the composition of the MPS-44, 50 and 60 membranes are not completely open, two patents of Kiryat Weizmann describe interesting procedures for the preparation of solvent stable membranes [82, 83]. In the former, porous polyacrylonitrile (PAN) membranes are crosslinked, for instance, by immersing them in a solution containing 1 % of metal alkoxides such as sodium ethoxide or 10 % of NaOH. The membranes are heated at 110 °C. UF-Membranes which are not soluble or swellable in DMF, NMP or DMSO are then obtained. If a cut off in the range of nanofiltration or reverse osmosis is required, the membrane is coated with a hydrophilic polymer, which is later crosslinked, or with polyfunctional reactants, which react forming a crosslinked coating. Some of the described coatings were based on polyethyleneimine and reactive dyes [84]. In a second patent [85], coatings of bromomethylated phenylene oxide were crosslinked with ammonia. An earlier patent [86] discloses the improvement of the solvent resistance of PAN membranes by a reaction with hydroxylamine, followed by treatment with cyanuric chloride and NaOH. The resulting membrane also has an improved resistance to compaction.

Carbon membranes are also described in the Kiryat Weizmann patent [82] starting from the same PAN membranes mentioned above. After immersion in an organic or inorganic base solution the membrane is heated at 110–130 °C, below the glass transition temperature, to induce a partial cross-linking and prevent plastic flow during heating at higher temperature. The membrane is then heated further at 250 °C for a few minutes and later in a non-reactive environment at 600–1000 °C for carbonization.

Koch also commercializes SelRO® membranes especially suitable for extreme pH conditions. Some of them are listed in Tab. 6.

Such membranes have been applied in the separation of heavy metals from acids and highly alcaline solutions, and in the recovery of alcaline solutions used in cleaning processes.

D-Series nanofiltration membranes produced by Desal/Osmonics work at very low pH levels. They have been used to recover heavy metals and clarify 35 % sulfuric acid feed streams or 25 % phosphoric acid streams. They have also been applied to permeate boric acid and reject radionuclides at a nuclear power station. Somicon is now announcing new membranes able to withstand up to 15 % NaOH at 60°C for nanofiltration (cut off 200-250 g/mol). The membranes are being applied to alcaline degreaseing baths and in the food sector. Also membranes for pH much below 1 with 90 wt % NaCl rejection are being supplied by Somicon /Nitto.

The ETNA membranes which were commercialized by Dow Danmark consisted of poly (vinylidene fluoride) (PVDF) porous supports with cellulosic coatings [87]. PVDF

Tab. 6: pH Stable SelRO® nanofiltration membranes

Membrane system	**Cut off (g/mol)**	**pH**	**Maximum temperature (°C)**
MPT 30	400	0–12	70
MPT 31	400	0–14	70
MPT 34	200	0–14	70
MPT 36	1000	1–13	70
MPS 31	450	0–14	70
MPS 34	300	0–14	70
MPS 36	1000	1–13	70

is soluble only in a few organic solvents such as dimethyl acetamide. Cellulose is very stable in organic and aqueous solvents. However, because of its low solubility, preparing cellulose membranes is not a trivial task. Stengaard [62] proposed the preparation of composite membranes by coating chlorotrifluoroethylene/vinylidene fluoride (CTFE/VF) or PVDF supports with hydroxyethylcellulose and hydroxypropylcellulose, which are water soluble. In order to fixate these materials on the membrane surfaces they have to be crosslinked and/or chemically bonded to the support. PVDF and CTFE/VF copolymer can be made reactive in the following way. Under highly alkaline conditions and elevated temperatures hydrogen fluoride/hydrogen chloride are set free while reactive groups and double bonds are formed. The support is then treated with a solution of hydroxyalkylcellulose in the presence of NaOH and a cross-linking agent such as 1,3-dichloro-2-propanol, which forms ether bonds with hydroxyalkylcellulose via the OH groups. A stable hydrophilic layer is formed on the top of the PVDF support. The coating may just hydrophilize the UF-membrane or close the pores bringing the cut-off in the range of nanofiltration. An Etna membrane with 1000 molecular weight cut off was reportted to have a pure water flux of 50–100 l/m^2 h at 40 °C and was stable between pH 1 and 12 (Petersen). Membranes of hydroxyalkylcellulose crosslinked with glutaraldehyde were discussed in the literature as being chemical resistant with cut-offs around 600 g/mol [44].

Polyetherketons are engineering thermoplastics with an exceptional combination of heat and chemical stability. However, their high insolubility in all common solvents, a property which assures the successful application of the membrane in chemical processes, inhibits their production by conventional solution casting methods. In order to bypass this difficulty, alternative preparation methods have been reported in the patent literature. One possibility is the partial sulfonation of PEEK with sulfuric acid and preparation of the membrane by coagulation from the sulfuric acid solution [88]. The final membrane characteristics are, however, affected since the sulfonated PEEK is now soluble in common solvents. Furthermore, sulfonated PEEK swells in aqueous solution, which prejudices the performance of the membrane in water. Membranes have been also prepared from blends of poly (aryl ether ketone) and poly(ether imide) (PEI) submitted to solvent leaching (of PEI) to form the pores [89]. A symmetric membrane with low porosity is formed. Ionics [90] proposed the preparation of membranes by casting from solutions in strongly protic, non-reactive acids such as methanesulfonic acid. Dow described [91] the extrusion of PEEK with a plasticizer, followed by coagulation in a non solvent bath and leaching of the plasticizer. Drawing before, during and/or after leaching improves the flux of the membranes.

Poly(phenylene sulfide) (PPS) is another chemically stable polymer. Analogously to the procedure for preparation of PEEK membrane, Dow proposed in a recent patent the preparation of PPS membranes by extrusion followed by leaching.

Polyimide membranes for ultrafiltration have long been the subject of Nitto patents [92]. Although unsoluble in many common solvents such as alcohols, ketones, ethers and esters, solutions in dimethyl formamide may be manufactured into membranes by casting/coagulation procedures. Polyimide membranes with high solvent resistance are claimed by Bend Research, by casting from polyamic acid solutions [93].

Porous polybenzimidazole (PBI) membranes were also developed in an attempt to overcome the temperature and chemical stability limitations of other membranes. Procedures for preparation of PBI membranes by phase inversion are long known [94]. The polymer can be dissolved in dimethyl acetamide and coagulated in a bath containing a mixture of solvent and non-solvent to hinder the excessive formation of finger-like cavities [95]. Dense PBI membranes, treated with phosphoric acid are now being considered for application in fuel cells [96].

Polyphosphazenes are also valuable as a membrane material with high chemical stability. They have been explored for ultra- and nanofiltration, pervaporation, gas separation [97] and more recently for application in fuel cells [98]. Although commercial membranes are not available, UF phosphazene membranes have been prepared by phase separation with cut offs between 70,000 and 500,000 g/mol and water fluxes up to 30 m^3/m^2 day MPa with mean levels of stability in acetone or hexane. Nanofiltration phosphazene membranes on ceramic support have been successfully used for the separation of organic dyes from isopropanol. The US Department of Energy, through its Office of Industrial Technology is supporting a wide spectrum of research on polyphosphazene membranes in the chemical and petrochemical industry. One topic of interest is, for instance, the separation of water from hydrocarbons by pervaporation.

A successful case also supported by the US Department of Energy was the treatment of waste water containing pigments and solvents with a combined UF/RO process. The membrane system was supplied by Zenon Environmental Systems. Ultrafiltration removed suspended solids and high molecular weight particles and reverse osmosis removed smaller impurities, during the treatment of waste water of PPG Industries, the world's largest producer of automotive and industrial coatings. The system reduced the amount of contaminated water requiring offsite disposal from 400,000 gallons to less than 20,000 gallons annually.

4.5 Membranes for microfiltration

Several of the polymers mentioned above for ultrafiltration can also be used for the preparation of microfiltration membranes by phase inversion. However, for the range of pore size useful for microfiltration, other procedures have also been successfully used for the preparation of commercial membranes. Among these are stretching, track-etching, leaching and sintering. Some commercially available MF membranes are shown in Tab. 7.

Tab. 7: Some commercially available membranes for microfiltration.

Millipore

Trade name	**Membrane material**	**Pore size (µm)**	**Porosity (%)**	**Chemical resistance**	**Max. operating temperature (°C)**	**Protein adsorption (mg/cm^2)**
Durapore	PVDF, hydrophilic	0.1–5.0	70–75	1–5	85	4
	PVDF	0.1–0.65		1–4		150
MF-Millipore	CA/CN	0.02–8	70–84	1–2	75	150
Fluoropore	PTFE on PP	0.2–3	70–85	1–5	130	
Mitex	PTFE	5–10	60–85	1–5	260	
LCR	PTFE, hydrophilic	0.5				
Isopore	PC	0.05–12		1–3	140	
	PET	0.2–5	8–14	1–4	140	

Chemical resistance:
1 Water solution pH 2–11
2 Alcanes, aromatic hydrocarbons, halogenated alcanes
3 Alcohols
4 Ketones, esters, organic acids
5 Concentrated strong acids and bases

PALL

Membrane units	**Membrane material**	**Removal rating (µm)**	**Chemical resistance**
PallCell®	Cellulose	8–35	
Ultipor® N66	Polyamide 6,6	0.1–0.2	alcohols, esters, cetones
N66® Posidyne®	PA 6,6 with positive charge	0.65–0.04	
Fluordyne® II	PVDF, hydrophilic	0.04–0.2	
Emflon®	PTFE with PP core		acids, bases, alcohols, esters, halogenated hydrocarbons, cetones
Emflon® II	PVDF	0.05–1	acids, <5% base sol., alcohols, esters, halogenated HC
Super Cheminert	PTFE/PFA	0.05–1	hot conc. acids, solvents, oxidizers
Ulti-Cheminert	PTFE/PFA	0.05–0.2	hot conc. acids, solvents, oxidizers

PALL Gelman

Trade name	**Membrane material**	**Pore size (μm)**	**Max. temp. (°C)**	**Water Flow (ml min^{-1}cm^{-2} at 0.7 bar)**	**Chemical resistance**
Supor	Polysulfone, hydrophilic	0.1–0.8	100	5 (0.2μm)	
HT Tuffryrn	Polysulfone, hydrophilic	0.2, 0.45	121	12 (0.2μm)	harsh aqueous solutions, alcohols
Versapor	Hydrophilic acrylic copolymer	0.2–3	88	17 (0.2μm)	
GN-4 Metricel	Hydrophilic mixed cellulose esters	0.8	74	145	
GH Polypro	PP, hydrophilic	0.2, 0.45	55	17 (0.2μm)	aqueous and aggressive organics
FP Vericel(TM)	PVDF	0.2, 0.45	100	3.5 (0.2μm)	
Nylasorb(TM)	Polyamide	1	180		
Nylaflo(TM)	Polyamide, hydrophilic	0.2, 0.45	100	8 (0.2μm)	high chemical resistance in esters, bases, alcohols
Metricel®Polypropylene	Polypropylene	0.1	82	1.5 (isopropanol)	aggressive solvents
Ion-exchange ICE450R	Polysulfone with sulfonic acid sites	0.45	100	21	
SB-6407	Polyethersulfone/ copolymer with quaternary ammonium sites	0.45	150	12	
Zefluor	PTFE on PTFE support	0.5–3			harsh chemicals
Teflon	PTFE with polymethylpentene	1–3			harsh chemicals
ZylonTM	PTFE	5			harsh chemicals

Desal

Trade name	**Membrane material**	**Pore size (μm)**	**pH**	**Applications**
J-Series	PVDF	0.30	2–11	removal of suspended solids, diatomaceous earth replacement, cationic ED paint recovery
E-Series	Polysulfone	0.04	2–11	post-treatment of ultrapure water, removal of suspended solids
K-Series	PTFE	0.10-3	2–11	process stream clarification, oil-water separation

Polypropylene and poly (tetrafluor ethylene)

Stretching is part of the preparation process both of the Celgard® and the Gore-Tex® membranes. Cold drawing has been described already in 1969 [99] for membrane preparation starting from crystalline polymers. Another preparation method is solvent stretching [100], where the precursor film is brought in contact with a swelling agent and stretched. The swelling agent is removed while the film is maintained stretched to render the film microporous. Other processes use sequencial "cold" and "hot" stretching steps [101].

The Celgard® membrane is made of polypropylene, which is a low cost and quite inert polymer. It is resistant under extreme pH conditions and is insoluble in most solvents at room temperature. It swells however in very apolar solvents such as carbon tetrachloride. No solvent is required for the preparation of the membrane. It involves the extrusion of PP films with high melt stress to align the polymer chains and induce the formation of lamellar microcrystallites when cooling. The film is then 50–300 % stretched just below the melting temperature. Under stress, the amorphous phase between the crystallites deforms, giving rise to the slit-like pores of the Celgard® membrane (Fig. 11). The film is then cooled under tension. PP is highly hydrophobic and several surface treatments have been proposed to improve the hydrophilicity of PP membranes. Incorporation of surfactants is used to make Celgard® membranes more hydrophilic.

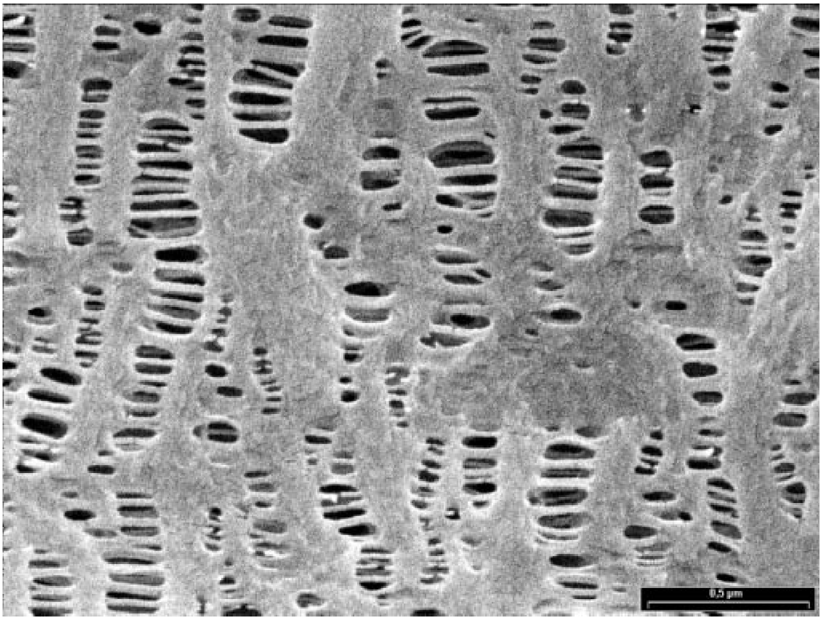


Fig. 11: Celgard® membrane.

Another commercial membrane prepared by stretching is Gore-Tex (Fig. 12). The polymer here is poly(tetrafluor ethylene), what makes the membrane extremely inert and thus convenient for processing even harsh streams. Processing PTFE is only possible by paste extrusion. In paste forming the polymer is mixed with a lubricant such as odorless mineral spirits naphtha or kerosene. The lubricant component is removed by heating up to 327 °C. Above this temperature, sintering would lead to a dense PTFE film. After lubricant removal, the PTFE film is submitted to an uniaxial or biaxial stretching, giving rise to an interconnected pore structure. The process was proposed by Gore [102] and the resulting porous film is today a successful product in the membrane and textile industry. For uniaxial stretching the unsintered film from the paste extrusion isfed to a machine with heating roles, where one role is driven faster than the previous one to input stress and induce the pore formation. The difference in speed determines the amount of stretch. Additionally in the Gore patent a biaxial stretching is performed using a pantograph.

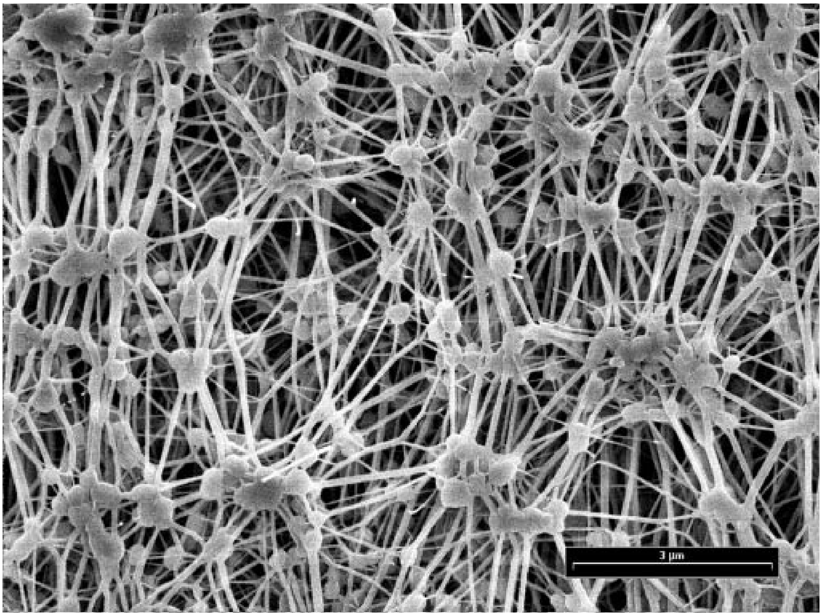


Fig. 12: Goretex® membrane.

A special characteristic of the Gore membrane is that, since PTFE is very hydrophobic, (liquid) water must not be allowed to wet the membrane and its transport is hindered. On the other hand, water vapor can freely pass through the micropores, making the film suitable for transpirating impermeable cloths. However due to their inertness, PTFE membranes are also interesting during the processing of aggressive streams. If the goal is the filtration of aqueous wastes the membranes should be modified to become hydrophilic. A solution is disclosed in a later Gore patent [103], mixing PTFE with silica and a surfactant to form the paste for the extrusion. To improve the adhesion of the filler to the PTFE matrix, the membrane, in the last step of preparation, is heated with a solution of dimethyl octadecyl chlorosilane in toluene.

Polycarbonate and poly (ethylene terephtalate)

Dense films of polycarbonate or poly(ethylene terephtalate) can be transformed into porous microfiltration membranes with very narrow pore size distribution (Fig. 13), by exposing them to fission fragments from radioactive decay with subsequent etching in alcaline solutions. The number of pores can be controlled by the length of exposure to the fission segments. The maximum pore density is limited by the fact that membranes become excessively brittle and radioactive at very high doses. The size of the pores is controlled by the etching conditions and the length of time in the etching bath. The shape of the nuclear pores (cylindric or conic) is determined by V, the relation between the rate of etching of the bulk membrane material and the rate of etching of the material along the high energy particle track. For instance, in poly (ethylene terephthalate) films tracked by argon ions, V = 10–100 and the pores are less cylindrical than in films tracked by xenon ions, for which V = 100–1000 [104].

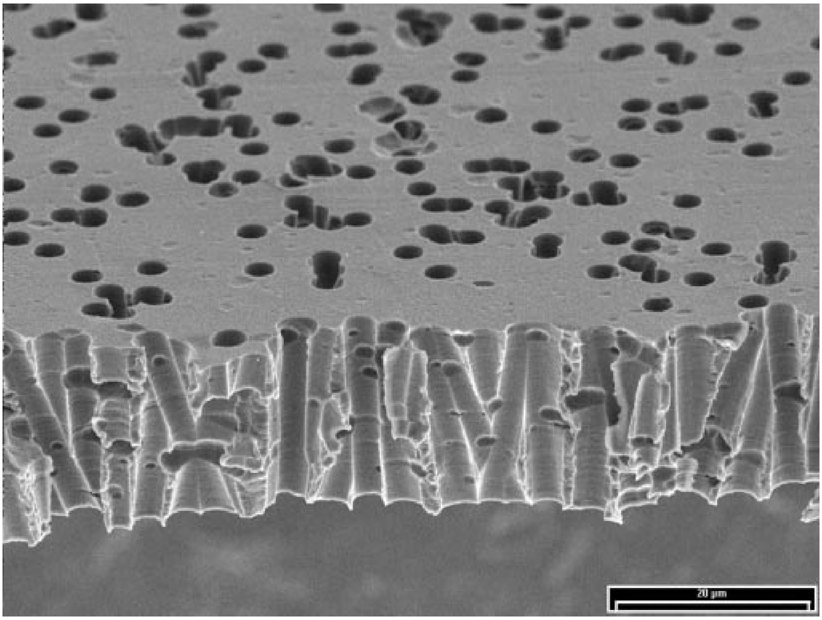


Fig. 13: Poly(ethylene terephthalate) membrane.

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5 Surface Modification of Membranes

Although membrane preparation has been reported concerning a large variety of polymers, it is often not possible to combine the best characteristics needed for the application, using just one polymer. It is frequently observed for instance, that polymers with the best solvent resistance or those which provide the most convenient pore structure are too hydrophobic to have an acceptable performance in the filtration of aqueous solutions. On the other hand, chemical modification of the polymer chain prior to membrane formation usually drastically changes the resulting pore structure. Therefore several procedures have been researched to chemically modify the surface of a previously formed porous membrane in order to increase the hydrophilic character or to allow functionalization and incorporation of polymer segments. These may improve selectivity, raise biocompatibility or bond catalytically active groups for membrane reactors. Chemical modification of polymer surfaces has been reviewed [105].

5.1 Chemical oxidation

In many cases hydrophilicity is the main goal of membrane surface modification. Surface oxidation is the simplest way to attain this goal. Several methods are available, including glow and corona discharge [106] and surface flaming, which are quite old but still very effective methods particularly in the case of polyolefins. Additionally one of the earliest surface treatments, still effective, is the exposure to oxidizing chemicals such as chromic acid, nitric acid or potassium permanganate, which lead to the formation of carbonyl, hydroxyl and carboxylic groups on the surface of polyethylene, polypropylene and polyesters.

One procedure for the modification of polypropylene membranes [107] consists of reacting the membrane in an aqueous solution of heated potassium peroxy disulphate to produce oxygen-centered radicals which are responsible for introducing hydroxyl groups. If the process is performed in the presence of monomers such as acrylamide, grafting takes place.

5.2 Plasma treatment

Plasma is a complex gaseous state of matter, consisting of free radicals, electrons, photons, ions, etc. Plasma can be generated by continuous electrical discharge in either an inert or a reactive gas. For membrane application, plasma can be used to improve the characteristics both of porous supports and of polymer films for gas separation. Several examples have been reviewed by Kramer et al. [108]. Porous membranes can be submitted to plasma treatment to achieve the following effects: (i) crosslinking of the top layer and reduction of pore size; (ii) introduction of functional groups to the surface or (iii) grafting and deposition of a thin selective layer on a porous substrate.

In the former instance, plasma treatment with inert gases such as argon or helium leads to ablation of the substrate material by the excited plasma molecules and then redeposition of the substrate material as a highly crosslinked layer on the surface. If the time of exposure is limited, a controlled reduction of pore size is obtained and a microfiltration membrane can be transformed into an ultrafiltration or even reverse osmosis membrane. Argon plasma was used to reduce the pores of polyethylene hollow fibers. It has been reported that helium plasma modifies the surface of porous polyacrylonitrile membranes, making them suitable for reverse osmosis.

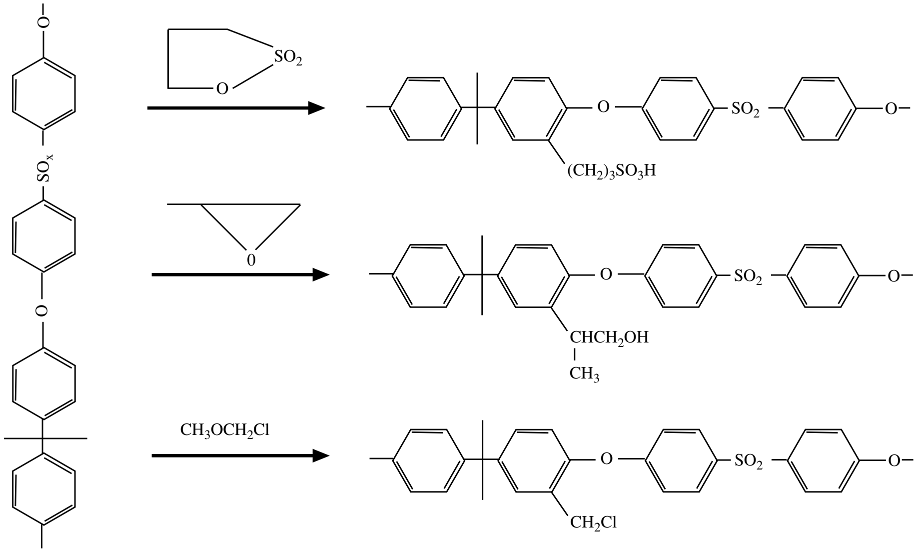
A second application is the incorporation of functional groups. Plasma treatment with air, oxygen and water vapor introduces oxygen-containing functional groups on the surface. Nitrogen, ammonia and alkyl amine plasmas introduce nitrogen-containing functional groups. Treatment of PAN and polysulfone membranes with helium/water plasma, as reported by Belfort and Ulbricht [109, 110], turns them hydrophilic and minimizes fouling. It is interesting to note that amino groups are for instance interesting to bind heparin and retard blood coagulation in membranes used in medical applications [108]. Ammonia plasma was also used to improve flux and selectivity of UF-polysulfone membranes [111]. Nitrogen and oxygen plasma have been used to improve the hydrophilicity of poly (vinyl chloride) membranes.

Hydrophilization can also be obtained by plasma-induced graft polymerization with the incorporation of hydrophilic monomers. The plasma is then generated from gaseous organic monomers which polymerize and eventually crosslink on the membrane surface. The conditions may also be adjusted to lead to a dense selective polymer coating. One advantage of the plasma treatment is the absence of solvents or any hazardous liquid. A weak point is the complexity of the coating, which is difficult to predict. Several examples are reported in the literature. Ulbricht and Belfort polymerized hydroxy ethyl methacrylate on polysulfone membranes. Acrylic acid was deposited on commercial membranes to improve solute rejection during the ultrafiltration of bleach effluents [112].

5.3 Classical organic reactions

The well-defined surface functionalization using classical organic reactions plays an important role in membrane development. In order to be susceptible to reaction, the polymer chain should contain double bonds, hydroxyl groups or benzene rings. An example is the modification of polysulfone by reaction with different chemicals to increase hydrophilicity.

The surface modification of polysulfone membranes has been reported by several authors [113, 114].



5.4 Polymer grafting

The covalent bonding of polymer segments and chains to porous supports can be achieved by polymer graft (Tab. 8), which is, to a great degree based on the free radical reaction of vinyl or acrylic monomers. Reactive sites on the polymer support, usually in the form of unpaired electrons, can be created by i) UV-irradiation in the presence of initiators such as benzophenone and the chosen monomer; ii) reactive sites are also thermally created as result of the decomposition of organic peroxides. The third alternative is iii) the generation of unpaired electrons by exposure to high-energy radiation, such as gamma- or electron-irradiation.

Grafting of hydrophilic vinyl monomers such as hydroxyethyl methacrylate on polysulfone and PAN membranes under UV exposure to make them less susceptible to foulinghas been described in the literature [122, 123].

Tab. 8: Different monomers and initiation methods for polymer grafting.

Monomer	Substrate	Reference
UV-Photoinitiated		
Acrylic acid	PE PP PET	115 116 117, 118
Glycidyl acrylate	PE PS PP	119, 120 120 120
Acrylamide	PE PP PET	115 116, 121 117, 118
4-Vinyl pyridine	PET	117
2-Hydroxy-ethylmethacrylate	PSU	122, 123
Thermally initiated		
Acrylamide	PE	124
Acrylic acid	PET	125
Methacrylic acid	PET	126
Acrylic acid/ maleic anhydride	PP	127
Glycidyl methacrylate	PP	128
Fluorinated acrylic	Polyester	129
High-energy irradiation initiated		
Acrylamide	PE LLDPE PP	130 (electron beam) 131 (electron beam) 132 (gamma ray)
Acrylic acid	PP	133 (gamma ray, plasma) 134 (gamma ray)
Fluoroalkyl methacrylate	PDMS	135 (plasma)
Vinyl pyrrolidone	TFB	136 (gamma ray)
Poly (ethylene imine)	PE, PET	137 (plasma)

PE = polyethylene, LLDPE = linear low density polyethylene,
PP = polypropylene, PS = polystyrene, PET = poly (ethylene terephthalate), PSU = polysulfone,
TFB = poly (tetrafluoro ethylene-hexafluoropropylene)

The incorporation of positive charges has decreased the fouling susceptibility of membranes even more effectively. This is the principle of the aromatic polyamide membrane series commercialized by Hydranauts as low-fouling composite membranes (LFC). Cationic charge-modified polyamide membranes are also commercially available from CUNO under the trademark ZETAPOR. Pall Corp. sells cationic charge-modified polyamide membranes under the trademark N66 POSIDYNE. There are different ways to make the membrane positively charged. A patent from Millipore [138] describes the surface modification of hydrophobic membranes by contacting them with a solution of polyamine epichlorohydrin containing quaternary or ternary ammonium functional groups and acrylate monomers which can polymerize under UV irradiation onto the surface. The CUNO membrane [139] is based on the procedure disclosed in the US Pat. 4473475 [140] for modifying polyamide membranes. Here a charge modifying agent such as tetraethylene pentamine is bonded to the hydrophilic sites of the membrane through a polyepoxide crosslinking agent. The membrane surface modifying polymers, disclosed in the Pall patent [141], are cationic, water-soluble, quaternary ammonium, thermosetting polymers such as the epoxy-functional polyamine epichlorohydrin.

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6 Gas Separation with Membranes

6.1 Introduction

The separation of gas mixtures with membranes has emerged from being a laboratory curiosity to becoming a rapidly growing, commercially viable alternative to traditional methods of gas separation within the last two decades. Membrane gas separation has become one of the most significant new unit operations to emerge in the chemical industry in the last 25 years [142]. The gas separation membrane module business for 2000 is estimated at $ 125 million with an annual growth rate of 8 %. Table 9 shows commercial applications and some of the major suppliers of membrane gas separation units.

Tab. 9 shows established applications in the field of membrane gas separation. One of the new and currently small applications as shown in Tab. 9 is natural gas dehydration. Problems related to this separation will be discussed in the last part of this chapter (basic process design considerations). Besides the well-established applications there are a number of emerging membrane gas separations. These are, for example, natural gas hydrocarbon dewpointing, olefin/paraffin separation and separation of hydrocarbon isomeres. These will be addressed in the following material section. The purpose of this chapter is to provide an overview of state of the art and emerging materials for gas separation membranes, to give some key features of integral asymmetric and composite membranes and finally to explain the influence of basic process parameters.

6.1.1 Materials and transport mechanisms

Organic polymers are the dominating materials for gas separation membranes. Many polymers exhibit a sufficient gas selectivity and they can be easily processed into membranes.

Palladium alloys are the only inorganic materials which are currently used for gas separation (ultra-pure hydrogen generation) on a commercial scale. However, during the last decade inorganic materials have been developed with exciting unmatched selectivities for certain gas mixtures and some of the inorganic membranes described in the scientific literature seem to be on the brink of commercialization. Table 10 shows relevant membrane materials for gas separation.

Tab. 9: Gas membrane applications and suppliers (adapted from "Economics of gas separation membranes", R.W. Spillman, in: Membranes separation technology. Principles and applications, Ed.: R.D. Noble, S.A. Stern, 1995, Elsevier Science.

Gas separation	**Application**	**Suppliers**
O_2/N_2	Nitrogen generation, oxygen enrichment	A/G Technology Permea (Air Products) Generon (Messer) IMS (Praxair) Medal (DuPont, Air Liquide) Aquilo (Parker Hannifin) Ube
H_2/Hydrocarbons	Refinery hydrogen, recovery	Air Products Air Liquide Praxair
H_2/CO	Syngas ratio adjustment	as above
H_2/N_2	Ammonia purge gas	as above
CO_2/Hydrocarbon	Acid gas treating, enhanced oil recovery, landfill gas upgrading	Kvaerner (Grace Membrane System) Air Products Ube
H_2S/hydrocarbon	Sour gas treating	as above
H_2O/hydrocarbon	Natural gas dehydration	Kvaerner Air Products
H_2O/air	Air dehydration	Air Products Ube
Hydrocarbons/air	Pollution control, hydrocarbon recovery	MTR, GMT, NKK
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery	MTR, GMT, SIHI

Tab. 10: Materials for gas separating membranes.

Organic polymers	**Inorganic materials**
Polysulfone, polyethersulfone	Carbon molecular sieves
Celluloseacetate	Nanoporous carbon
Polyimide, polyetherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silicia
Polyphenyleneoxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	
Polyvinyltrimethylsilane	

6.1.2 Organic polymers

A number of excellent books and reviews have been published on the subject of polymeric gas separating membranes, which are recommended to the interested reader [143, 144, 145, 146, 147, 148, 149]. It is the purpose of this chapter to supply the reader with a basic background which is important in the understanding of the transport mechanism of gases through polymers, to introduce those polymers which are currently of commercial importance and finally to give an outlook on interesting developments in this field.

6.1.3 Background

The simplest model used to explain and predict gas permeation through non-porous polymers is the solution-diffusion model. In this model it is assumed that the gas at the high pressure side of the membrane dissolves in the polymer and diffuses down a concentration gradient to the low pressure side, where the gas is desorbed. It is further assumed that sorption and desorption at the interfaces is fast compared to the diffusion rate in the polymer. The gas phase on the high and low pressure side is in equilibrium with the polymer interface. The combination of Henry's law (solubility) and Fick's law (diffusion) leads the to the equation

$$J = \frac{D * S * \Delta p}{l} \tag{1}$$

which can be simplified to

$$J = \frac{P * \Delta p}{l} \tag{2}$$

where D is the diffusion coefficient of the gas in the polymer, S is the gas solubility, Δp is the pressure difference between the high and low pressure side, l is the membrane thickness and P is the permeability coefficient[1]. As can be seen from (1) and (2) the permeability coefficient P is the product of D (a kinetic term) and S (a thermodynamic term).

$$P = D * S \tag{3}$$

---

[1] The permeability coefficient is most commonly given in Barrer, defined as 10^{-10} $cm^3 cm/cm^2 s$ cm Hg and named after R. M. Barrer. The correspondend SI unit is mol m/m2s Pa (1Barrer= 0.33×10^{-15}mol $m/m^2 s$ Pa).

The selectivity of a polymer to gas A relative to another gas B can be expressed in terms of an ideal selectivity α_{AB} defined by the relation

$$\alpha_{AB} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \tag{4}$$

The ratio D_A/D_B can be viewed as mobility selectivity and the ratio S_A/S_B as solubility selectivity. For a given gas pair mobility and solubility selectivity depend on the chemical and physical properties of the polymeric material. Excellent reviews on relationships between polymer structure and transport properties of gases have been given by Stern, Paul and Freeman [147, 150, 151]. Some general rules are useful for a first understanding. The diffusion coefficient D always decreases with increasing size of the molecule. The extent of this decrease is generally dependant on the flexibility of the polymer backbone. The more rigid the polymer structure the higher the mobility selectivity will be for a given gas pair. The mobility selectivity is dominant for most glassy polymers. Hence, the transport of smaller molecules is favored. On the other hand the solubility of gases generally increases with molecular size, because the intermolecular forces between gas and polymer increase. Most rubbers show a low mobility selectivity due to their flexible polymer chain but their ability to separate gases is dominated by their solubility selectivity. Thus large organic vapor molecules can permeate much faster through some rubbers than smaller gases like oxygen or nitrogen. This is depicted for silicone rubber in Fig. 14.

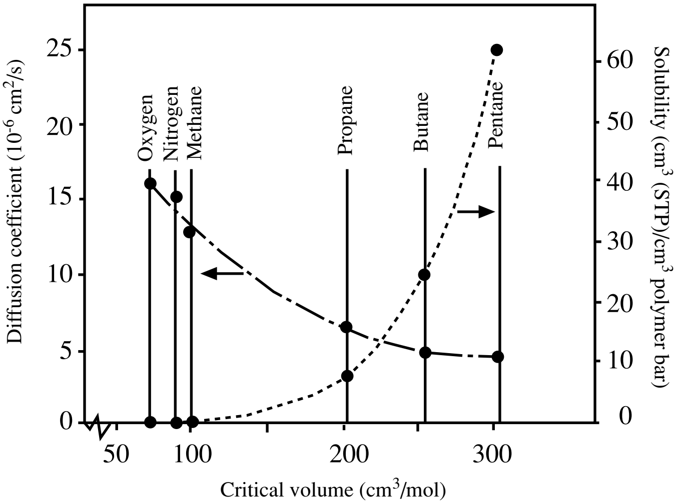


Fig.14: Diffusion and solubility coefficients of different gases in silicone rubber at 30°C [152, 153, 154] vs. the critical volume.

It can be seen that the diffusion coefficient of the large pentane molecule is 3.6 times smaller than the diffusion coefficient of oxygen. However, the solubility of pentane is about 200 times larger than the solubility of oxygen. This solubility selectivity outnumbers the reverse diffusion selectivity. As a result silicone rubber is much more permeable for pentane than for oxygen.

Contrary to rubbers glassy polymers usually show a preferred permeability to smaller molecules. The mobility selectivity is much higher than the reverse solubility selectivity. This is shown in Fig. 15 with the polyimide Matrimid (Ciba Geigy).

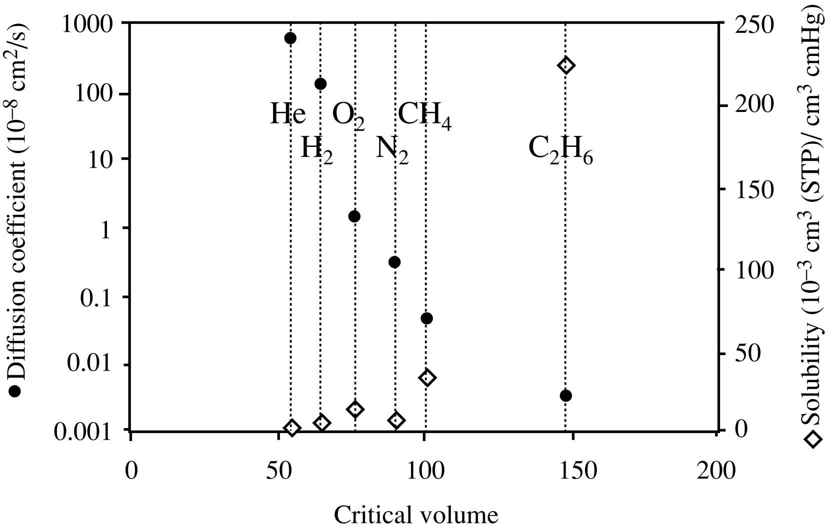


Fig. 15: Diffusion and solubility coefficients of different gases in Matrimid at 30°C vs. the critical volume.

6.1.4 Polymers for commercial gas separation membranes

During the last two decades dozens of new polymers have been described in the literature, which have been developed for gas separation. The largest group among these are probably polyimides [155]. In spite of these efforts less than 10 polymers are used for industrial gas separations. Nearly all of these are technical polymers developed for totally different applications. “Designer polymers” were either too expensive or their advantage over commercial polymers were not sensational enough or they did not show the expected performance in real applications. The latter is especially true for modified (fluorinated) polyimides. Some of the 6FDA-based polyimides showed tremendous separation abilities in the laboratory but failed in real life due to plastizisation or physical aging. Table 11 gives a list of polymers which are of practical importance for gas separation.

Tab. 11: Gas permeabilities of gas separation polymers.

	Permeability at 30°C (Barrer*)				
Polymer	**H_2**	**N_2**	**O_2**	**CH_4**	**CO_2**
Cellulose acetate	2.63	0.21	0.59	0.21	6.3
Ethyl cellulose	87	8.4	26.5	19	26.5
Polycarbonate, brominated		0.18	1.36	0.13	4.23
Polydimethylsiloxane	550	250	500	800	2700
Polymide (Matrimid)	28.1	0.32	2.13	0.25	10.7
Polymethylpentene	125	6.7	27	14.9	84.6
Polyphenyleneoxide	113	3.81	16.8	11	75.8
Polysulfone	14	0.25	1.4	0.25	5.6

* 1 Barrer = 10^{-10}cm^3 cm/cm^2 s cmHg

Cellulose acetate, polysulfone and polyimides are by far the most important polymers for gas separation membranes. When we look at the volume streams treated, the old-fashioned cellulose acetate is probably still the dominating polymer. The company Kvaerner Process Systems alone, which has acquired Grace Membrane Systems, has sold or operates membrane plants with CA-membranes for carbon dioxide separation for a total stream of more than 5 Mio m^3 (STP)/day. The only polymer in Tab. 11, which is especially designed for gas separation, is the brominated polycarbonate (tetra-

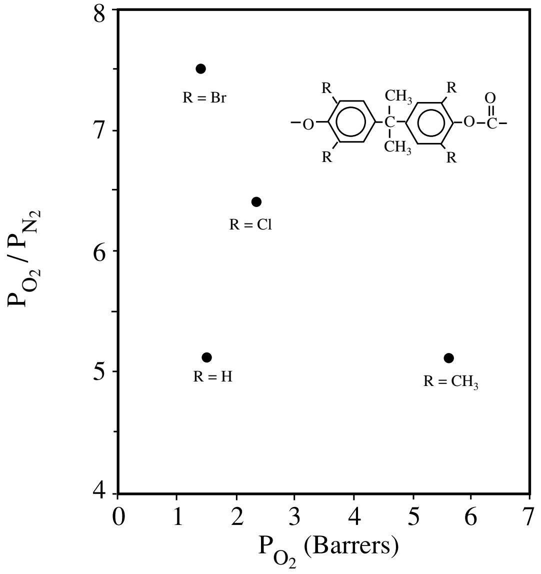


Fig. 16: Selectivity vs. permeability for O_2/N_2 for various polycarbonates at 35°C and 1 bar. [156] (reproduced by permission of Elsevier Scientific Publishers).

bromopolycarbonate). It was shown by Paul and coworkers [156] that this relatively simple modification led to an impressive increase in the oxygen/nitrogen separation factor without loss of permeability (see Fig. 16)

6.1.5 Ultra-high free volume polymers

Because the so-called ultra-high free volume polymers aroused much interest during the last 10 years, they will be briefly described in this introductory chapter. The publication of the physical properties of poly (1-trimethylsilyl-1-propyne) (PTMSP) in 1983 [157] aroused much interest in the field of membrane research. Up to this time it has been believed that the rubbery poly (dimethyl siloxane) has by far the highest gas permeability of all known polymers. Very surprisingly, the glassy PTMSP showed gas permeabilities more than 10 times higher than PDMS. This could be attributed to its very high excess-free volume and the interconnectivity of the free volume elements. Since then a number of high free volume polymers exhibiting extraordinaryly high gas permeabilities have been synthesized. Two of these are under extensive investigation and are currently being studied for gas separation on a pilot scale. These are Du Pont' s 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluorethylene copolymer (Teflon AF 2400®) and poly (4-methyl-2-pentyne) (PMP). All three polymers PTMSP, PMP and Teflon AF2400 are glassy with glass transition above 230°C and have a very high fractional free volume (FFV). Figure 17 shows the chemical structure and fractional free volume of these three polymers.

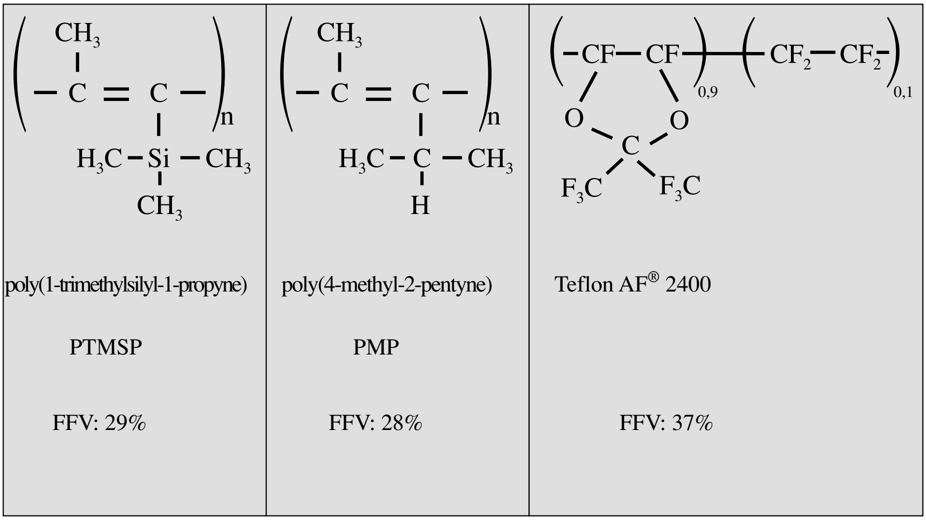


Fig. 17: Chemical structure and fractional free volume of PTMSP, PMP and Teflon AF24000.

Table 12 shows the oxygen permeability and oxygen/nitrogen selectivity of PTMSP, PMP and Teflon AF2400 in comparison with other polymers.

Tab. 12: Oxygen permeability and oxygen/nitrogen selectivity of high free volume polymers in comparison with conventional polymers.

Polymer	**Oxygen permeability (Barrer)**	**Oxygen/nitrogen selectivity**
PTMSP	**9700**	**1.5**
PMP	**2700**	**2.0**
Teflon AF2400	**1300**	**1.7**
PDMS	600	2.2
Polymethylpentene	37	4.2
Polyphenyleneoxide	17	4.4
Ethylcellulose	11	3.4
Polycarbonate	1.4	4.7

Although the PMP was already synthesized in 1982 [158], its high gas permeabilities were first published 1996 by Pinnau et al. [159] at MTR, Menlo Park. MTR is currently evaluating the performance of PMP membranes for hydrocarbon separation. An attractive application of membranes in this field is natural gas hydrocarbon dewpointing. This means the separation of higher hydrocarbons like butane present in natural gas from methane. Table 13 shows the performance of PTMSP and PMP membranes for the separation of a methane/butane mixture.

Tab. 13: Mixed gas permeation properties of PTMSP and PMP. Feed: 2 % butane in methane, feed pressure: 10 bar, permeate pressure: atmospheric, temperature: 25 °C From: I. Pinnau et al. In: Polymer membranes for gas and vapor separation, ACS Symposium Series 733 (1999), 56–67.

Polymer	**Permeability (Barrer)**		**Mixed-gas selectivity**	**Mixed-gas/pure gas**
	n-C_4H_{10}	**CH_4**	**n-C_4H_{10}/CH_4**	**CH_4 permeability ratio**
PTMSP	53 500	1 800	30	0.1
PMP	7 500	530	14	0.2

Although the permeability and selectivity of PMP is significantly lower compared to PTMSP , its performance for hydrocarbon separation is still superior to all other known polymers. The advantage of PMP lies in its much better chemical stability. In contrast to PTMSP it is not soluble in linear saturated hydrocarbons. With a mixed gas selectivity of butane over methane of 14, the PMP shows a much better performance than poly (dimethyl-siloxane), for which a selectivity of about 5 has been determined under similar conditions [160]. PMP has a poor pure gas selectivity for butane/methane separation, but in the presence of butane the methane permeability drops by a factor of 5. This effect is well known for the gas permeation through nanoporous solids, the condensable gas is selectively adsorbed on the pore walls, thus hindering the passage of the smaller molecules. It is believed that in a similar way the extraordinarily high excess free volume of the "super glassy" polymers can be occupied by condensable gases.

It will be quite interesting to observe which class of polymers will finally be applied for the attractive field of hydrocarbon dewpointing of natural gas. The superglasses like PMP show the highest selectivities and fluxes. However, due to their double bonds their chemical stability remains uncertain and they might be prone to physical aging, which is the irreversible absorption of components with high boiling points. Rubbery polymers like PDMS on the other hand are stable under natural gas conditions. However they loose selectivity under high partial pressure of higher hydrocarbons.

The third polymer listed in figure 4 has a very different structure in comparison with the polyacetylenes. The Teflon AF2400 is a perfluorinated random copolymer composed of 13 mol % tetrafluoroethylene and 87 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole. Its extraordinarily high gas permeability was first described by Nemser and Roman [161]. Composite membranes fabricated from this polymer are currently being tested on a pilot scale by Compact Membrane Systems, Wilmington. An attractive application seems to be the production of oxygen-enriched or oxygen-depleted air for mobile diesel engines [162] and the separation of supercritical carbondioxide [163].

6.1.6 Inorganic materials for gas separation membranes

The current market for inorganic membranes for gas separation is extremely small. One of the few commercial applications are small scale palladium membrane systems to produce ultrapure hydrogen for specialized applications. They are marketed by Johnson Matthey and Company. It is not believed that the market share of inorganic membranes will increase significantly in the near future. The main obstacle is their high price and some principle difficulties during reproducible large-scale production. On the other hand fascinating research results have been published in the recent past such as a propene/propane mixed gas selectivity of more than 40 with carbon molecular sieve membranes [164] or unmatched selectivities for carbondioxide/methane separation with ceramic membranes [165]. The interested reader is referred to some good reviews on inorganic membrane materials [166,167,168].

In this chapter three examples of inorganic membranes will be discussed, which might find industrial applications in the future.

6.2 Nanoporous carbon membranes

Nanoporous carbon membranes were one of the highlights in membrane development for gas separation during the last decade. They can be produced by different methods. The most advanced membranes of this kind have been produced by Air Products first published 1993 [169]. Air Products called this membrane Selective Surface Flow (SSF™) membrane.

It consists of a thin layer (2–3µm) of a nanoporous carbon matrix (5–7 Å pore diameter) supported on the bore side of a macroporous (< 1µm pore diameter) alumina tube. The membrane is produced by: (a) coating the bore side of the tubular support with a thin uniform layer of a poly(vinylidene chloride-acrylate) terpolymer latex containing small polymer beads in aqueous emulsion, (b) drying the coat under N_2 at 50 °C, (c) heating under a dry N2 purge to 600 °C for carbonizing the polymer, and (d) finally passivating the nascent carbon film by heating in an oxidizing atmosphere at 200–300 °C. The resulting membranes have quite defined pores in the 5 to 8 Å range. They are especially well suited for the separation of hydrogen/hydrocarbon mixtures. The remarkable point is that they exhibit a preferred permeability for higher hydrocarbons over hydrogen. Table 14 gives some permeability data from the original paper.

Table 14: Gas separation properties of nanoporous carbon membrane.

Gas	**Pure gas permeability (Barrer)**	**Mixed gas permeability**	**Mixed gas selectivity**
H_2	130	1.2	–
CH_4	660	1.3	1.1
C_2H_6	850	7.7	5.1
C_3H_8	290	25	21
C_4H_{10}	155	110	94

41.0 % H_2, 20.2 %CH_4, 9.5 % C_2H_6, 9,4 % C_3H_8, 19.9 % C_4H_{10}
from: M.B. Rao, S. Sircar, J. Membrane Sci., 85 (1993)253

As can be seen from the table the pure gas selectivities of the nanoporous carbon membrane are quite low, e.g. 1.19 for butane/hydrogen. However, for the mixture given in Table 14 the butane/hydrogen selectivity increases to 94. The reason for this is that the butane is selectively absorbed over hydrogen at the carbon pore wall and because the pores are so small the pathway for hydrogen is blocked. This effect of selective surface flow and pore blocking was first observed by Barrer and coworkers [170]. Due to its unmatched selectivity the nanoporous carbon membrane looks very attractive for hydrogen enrichment of refinery off-gases with low hydrogen content, e.g. FCC (fluidized catalytic cracker) off-gases. It is much more attractive than hydrogen selective membranes, because the hydrogen remains on the high-pressure side of the membrane and can be fed into a pressure swing unit for further purification. The drawback of the nanoporous carbon membrane is that water vapor and pentane and higher hydrocarbons should be removed before the membrane separation because they absorb very strongly in the membrane pores. Air Products SSF™-membrane is now being field-tested at different refinery sites [171].

6.3 Perovskite-type oxide membranes for oxygen separation

It has been known for a long time that certain dense ceramic materials are good conductors of oxygen at elevated temperatures. Oxygen transport through an ionic conductor is a result of oxygen ionic conduction mechanisms that involve oxygen defects such as lattice vacancies. One of the best known ceramic oxygen conductors is yttria-doped zirconia, which is widely used in high temperature oxygen sensors. Oxygen is transported through these materials as O^{2-} ion. Hence, when oxygen permeates through these materials there must be a flow of electrons in the opposite direction. Oxygen conducting ceramics like doped zirconia are good oxygen conductors but poor electronic conductors. The electronic conductivity of yttria stabilized zirconia is three to four orders of magnitude lower than its ionic conductivity. The oxygen can be pumped through the material by an external electrical field. However, a simple calculation reveals that this is not economic for oxygen separation due to the high electricity consumption. The situation changes when the ceramic material is a good conductor for both – oxygen ions and electrons. These materials are referred to as ionic-electronic mixed conductors. With these a high oxygen flux can be obtained without an external electrical field. Fig. 18 shows schematically the two types of oxygen ion transport membranes.

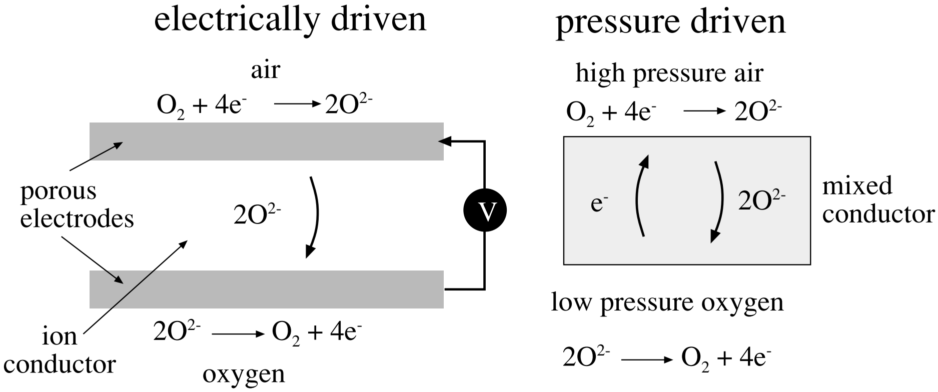
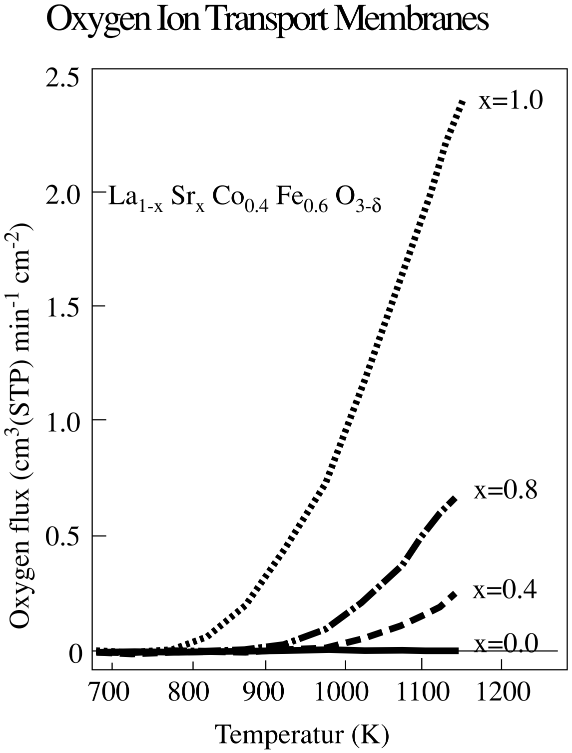


Fig. 18: Types of oxygen ion transport membranes.

One of the first papers which stimulated large interest in this research was published in 1985 by Teraoka et al. [172]. One of the figures of this pioneering paper is given here (Fig. 19).



Yamazoe et al., Chemistry Letters 1985, 1743

Fig. 19: Temperature dependence of the rate of oxygen permeation through perovskite membranes.

It may be deduced from Fig. 19 that, with a specific composition of the ceramic, an oxygen flux of up to 2.4 cm^3/min cm^2 could be obtained at a oxygen partial pressure difference across the membrane of 0.21 bar. The membrane thickness was 1mm. If one uses these data to calculate the permeability a tremendous value of 2.5 million Barrer is obtained. This is, of course, not totally correct because the oxygen flux through these membranes is not direct proportional to the oxygen partial pressure difference and is also not inversely proportional to the membrane thickness. At layers below 0.3 mm surface reactions become rate limiting. But even 0.5 mm thick membranes exhibit an oxygen flux at high temperatures which is orders of magnitude higher than the flux through the best polymeric membranes. The promising prospect of these membranes is not in the first place the production of oxygen, but their application in membrane reactors for the partial oxidation of natural gas, which is schematically shown in Fig. 20.

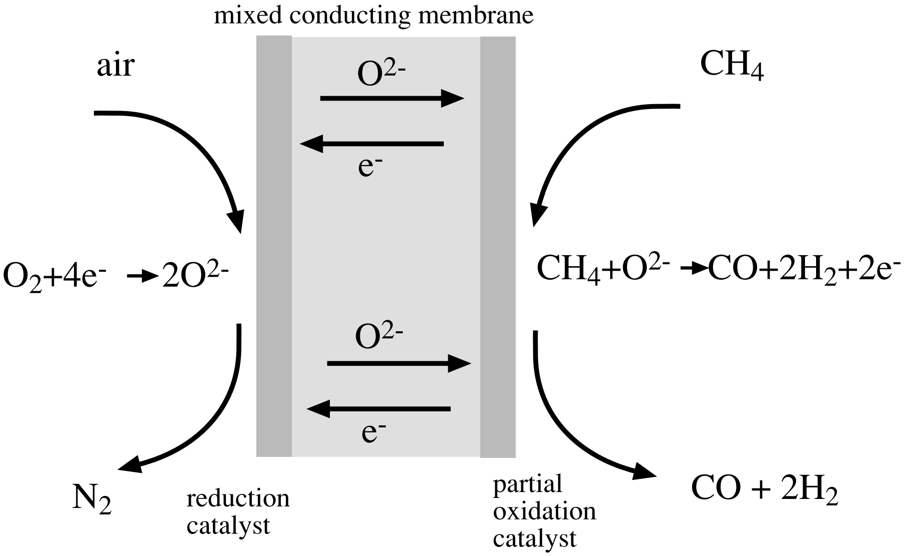


Fig. 20: Ion transport membrane mediated partial oxidation of methane.

The mixed conducting membrane eliminates the cryogenic air separation plant and it forms a safety barrier between the natural gas and air. The membrane becomes more productive in a configuration like this, because the slow oxygen desorption at the permeate side is enhanced by the chemical reaction. The big challenge for the future is the economic scale up of membrane production and the gas tight potting for temperatures above 700 °C.

The perovskite type ceramic membranes have attracted much attention from major chemical and petrochemical companies in the USA. Companies currently involved in the development of the mixed conducting ceramic membranes include AirProducts, Praxair, BP and Amoco. Many believe that the mixed conducting membrane technology will represent a major breakthrough in industrial application of inorganic membranes.

6.4 Mixed matrix membranes

Molecular sieves such as zeolites or carbon molecular sieves show a much higher selectivity for many gas mixtures than polymeric membranes due to their very defined pore sizes. For example it can be calculated from reported sorption and diffusivity data that zeolite 4A has an O_2-permeability of 0.77 Barrer and an O_2/N_2 selectivity of approximately 37 at 35°C [173]. The preparation of defect-free zeolite layers on a large scale is extremely difficult and it seems doubtful that this will ever be achieved at a competitive price. However, the combination of the superior gas selectivities of molecular sieves with the processibility of polymeric membranes have attracted many researchers.

The hybrid membranes consisting of inorganic molecular sieves and polymers are often referred to as mixed matrix membranes [174].

It was believed for a long time that the incorporation of a molecular sieve in a polymer matrix does not change the polymer selectivity under steady state conditions. Hennepe, from the university of Twente, proved for the first time that the incorporation of silicalite in PDMS increased the ethanol/water selectivity significantly under steady state conditions [175] in pervaporation experiments. Later it was shown by Jia et al. [176] that using the same approach (silicalite in PDMS) the gas selectivity could be also changed due to a molecular sieving effect. However, the effects were too small to be of any interest for practical applications. One of the fundamental questions of this concept is how the permeability of the polymer should match with the molecular sieve permeability. Koros proposed to use the following equation for an ideal modelling of the mixed matrix permeability:

$$P_{eff} = P_c \frac{(P_d + 2P_c - 2\phi(P_c - P_d))}{(P_d + 2P_c + \phi(P_c - P_d))}$$

where P_{eff} is the effective permeability, ϕ is the volume fraction of the dispersed phase, and the subscripts d and c refer to the dispersed and continuous phases, respectively. This equation was first derived by Maxwell to calculate the electric conductivity of a metal in which small spheres of a second metal are dispersed [177]. If this equation is used to calculate the selectivity of a mixed matrix membrane we obtain

$$\alpha_{eff} = \frac{\alpha_c(1/P_{c1} + 2/P_{d1} - 2\phi(1/P_{d1} - 1/P_{c1})(\alpha_c/P_{c1} + 2/P_{d2} + \phi(1/P_{d2} - \alpha_c/P_{c1}))}{(1/P_{c1} + 2/P_{d1} + \phi(1/P_{d1} - 1/P_{c1})(\alpha_c/P_{c1} + 2/P_{d2} - 2\phi(1/P_{d2} - \alpha_c/P_{c1}))}$$

where α_c is the selectivity of the continuous phase (the polymer) and the indices 1 and 2 refer to gas 1 and 2.

This equation looks complex at first sight but it allows the plotting of the selectivity of a mixed matrix membrane versus the polymer permeability, when the other parameters are fixed. An example is given in Fig. 21. In this example a 4A zeolite with an estimated O_2/N_2 selectivity of 37 and an O_2 permeability of 0.77 Barrer has been dispersed in polymer matrix with a O_2/N_2 selectivity of 7. The volume fraction of the zeolite is 0.60. The plot reveals that a maximum selectivity of the mixed matrix membrane is obtained in this case, when the polymer permeability is slightly higher than the zeolite permeability. When the polymer permeability becomes too high the selectivity of the mixed matrix membrane approaches the polymer selectivity. Hence the above equation gives a theoretical estimation of the selectivity of a mixed matrix membrane and it gives an idea of how the permeability of molecular sieve and polymer should match. The practical challenge is to improve the compatibility between inorganic molecular sieves and glassy polymers in order to eliminate gas diffusion pathways at the interface between polymer and zeolite. Once this problem is solved using nano-sized zeolite crystals the mixed matrix membranes might become an attractive alternative to polymeric membranes for commercial gas separation.

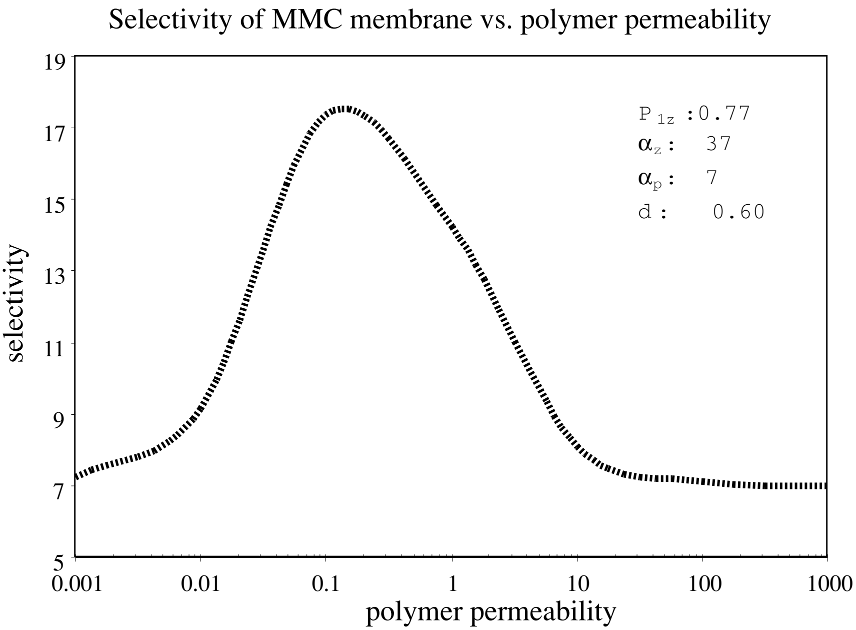


Fig. 21: Selectivity of a mixed matrix membrane vs. polymer permeability, zeolite O_2/N_2 selectivity 37, zeolite oxygen permeability 0.77 Barrer, polymer selectivity 7, zeolite volume fraction 0.60.

6.5 Process design

In this chapter some fundamental equations are given, which allow a first design of a one stage membrane separation unit. Questions to be answered are: what is the maximum enrichment, which can be achieved with a membrane of a given selectivity? How is the separation performance influenced by feed and permeate pressure? It will be explained why for some applications a high selective membrane will be outperformed by a membrane with a lower selectivity.

For the following we look at a simple gas separation unit with two components, which is illustrated in Fig. 22.

One parameter, which does of course determine the gas enrichment, is the membrane selectivity α, which is a membrane property and defined here as $\alpha = P_2/P_1$with P_2 and P_1 as permeability coefficients for gas 2 and 1. Equally important are two process parameters the stage cut θ and the pressure ratio ϕ. The stage cut is defined as ratio permeate flow/feed flow and the pressure ratio is the ratio of total feed pressure to total permeate pressure. For the sake of simplicity we start with a stage cut close to zero, i.e. there is no concentration difference between feed and retentate. The maximum enrichment of the faster component 2 can now determined easily. For the maximum enrichment the maximum driving force is needed, i.e. the permeate pressure can be neglected when compared to the feed pressure. The flux of component 1 is proportional to its

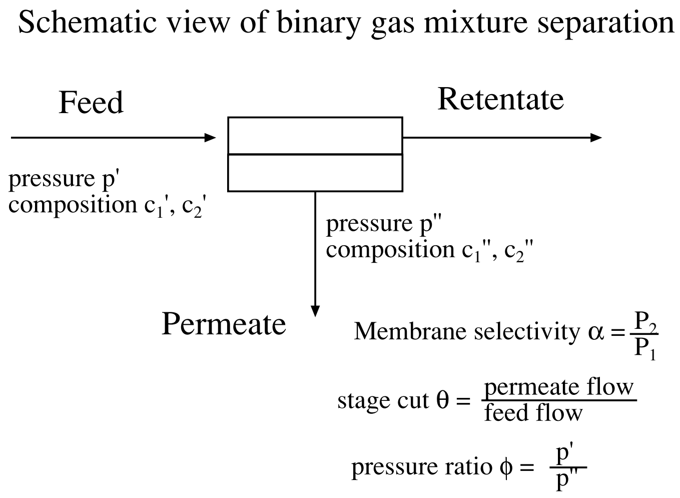


Fig. 22: Model gas separation unit with two components.

volume fraction on the feed side, for component 2 we have, as an additional factor the membrane selectivity.

$$J_1 = const. \times c_1' = const. \times (1 - c_2')$$
$$J_2 = const. \times \alpha \times c_2'$$

The concentration of component 2 on the permeate side must be equal to the flux J_2 of component 2 divided by the total flux $J_1 + J_2$. Combining equations 1 and 2 then yields

$$c_2'' = \frac{c_2' \times \alpha}{1 + c_2'(\alpha - 1)} \tag{3}$$

This simple equation gives the maximum possible enrichment of one gas of a two component mixture when separated by a membrane with a selectivity of a. The equation becomes more complex when the permeate pressure cannot be neglected [178]. Following the simple solution-diffusion model the gas fluxes for gas 1 and 2 through the membrane are

$$J_1 = \frac{P_1(p_1' - p_1'')}{l} \tag{4}$$

and

$$J_2 = \frac{P_2(p_2' - p_2'')}{l} \tag{5}$$

where P_1 and P_2 are the permeabilities of component s 1 and 2, l is the membrane thickness, and p_1', p_2'' and p_1'', p_2'' are the partial pressures of the two gases in the feed and permeate streams, respectively. The total gas pressure is equal to the sum of the partial pressures, i.e.

$$p' = p_1' + p_2' \tag{6}$$

$$p'' = p_1'' + p_2'' \tag{7}$$

with

$$c_2' = p_2' / p' \qquad c_2'' = p_2'' / p'' \tag{8}$$

and

$$J_1 / J_2 = c_1''/(1 - c_1'') = (1 - c_2'') / c_2'' \tag{9}$$

Combining equations (4–9) then yields the expression

$$c_2'' = 0.5\phi \left[c_2' + \frac{1}{\phi} + \frac{1}{\alpha - 1} - \sqrt{\left(c_2' + \frac{1}{\phi} + \frac{1}{\alpha - 1} \right) - \frac{4c_2'\alpha}{\phi(\alpha - 1)}} \right] \tag{10}$$

Equation 10 gives the concentration of the faster permeating gas in the permeate stream as a function of the membranes selectivity and the pressure ratio across the membrane. It breaks down into two limiting cases. At high driving forces when the pressure ratio is much higher than selectivity ($\phi >> \alpha$) equation 10 reduces to equation 3. We call this a selectivity controlled region, because the enrichment is now independent of the pressure ratio. When on the other hand, the pressure ratio becomes much smaller than the selectivity ($\phi << \alpha$), equation 10 reduces to

$$c_2'' = c_2'\phi \tag{11}$$

The enrichment is now independent of the membranes selectivity. Hence, this is the pressure ratio limited region. There is, of course, an intermediate region between these two limiting cases where both the presure ratio and the membrane selectivity affect the degree of separation. This is illustrated in Fig. 23, in which the calculated permeate concentration is plotted versus pressure ratio for a membrane with a selectivity of 200.

For numerous technical applications the pressure ratio does not exceed 10 or 20. An example is the separation of organic vapors, where a typical pressure ratio is about 10. Fig. 24 shows a plot of permeate concentration versus selectivity at a pressure ratio of 10. The plot reveals that an incrase of the selectivity above 40 does not increase the enrichment significantly. The highest permeate concentration achievable in this example is 5 % as predicted by equation 11.

The process might not only not benefit from a high selective membrane, but a too selective membrane might even be a disadvantage. This will be demonstrated with a

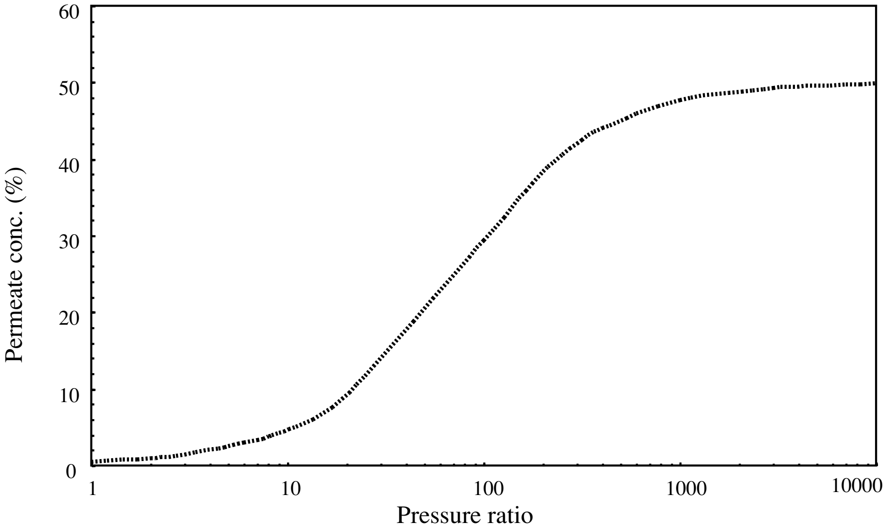


Fig. 23: Calculated permeate concentration for a membrane with a selectivity of 200 as a function of pressure ratio. The feed concentration is 0.5 %.

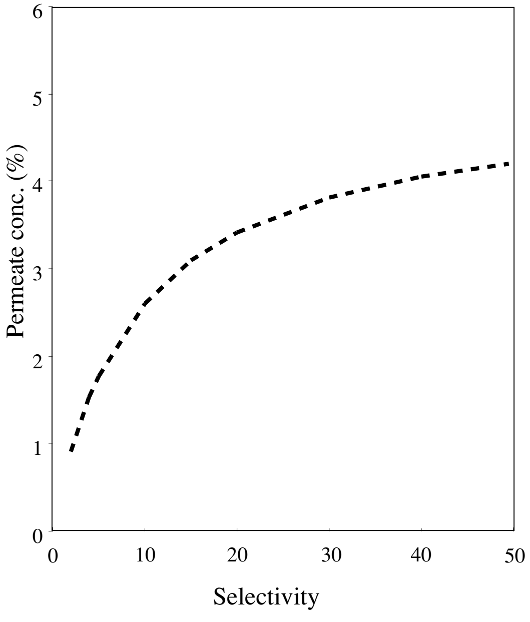


Fig. 24: calculated permeate concentration versus membrane selectivity for a pressure ratio of 10, feed concentration 0.5 %.

simple model calculation concerning natural gas dehydration. Natural gas dehydration is one of the emerging applications of membrane-based gas separation. The permeation of water vapor through polymers has one peculiarity. When plotting gas permeability versus selectivity for different polymers a general tendency exists: the more selective a polymer is the lower is its permeability, as shown in the famous Robeson plots [179]. Fig. 25 displays a plot of water vapor/nitrogen selectivity versus water permeability for a number of polymers. The afore-mentioned tendency does not hold here. On the contrary, many very selective polymers also have a very high permeability[1]. Numerous polymers are available with water vapor selectivities of 5000 and more.

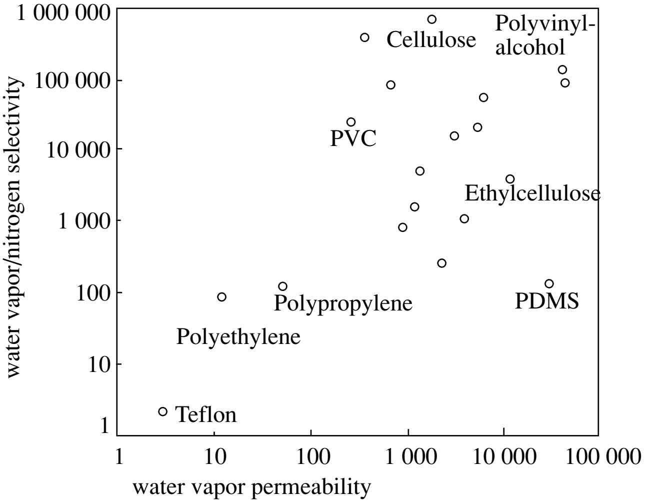


Fig. 25: H_2O/N_2-selectivity versus permeability for various polymers.

For the following calculation a two component water vapor/methane mixture has been assumed with 0.2 % water vapor. The membrane unit shall reduce this water content by one order of magnitude; i.e. the retentate water concentration has been set to 0.02 %. The simple equation 10 cannot be applied, the equations first derived by Weller and Steiner [180] have been used for the calculation of methane loss and the equation of Saltonstall [181] for calculation of membrane area. The methane loss is simply defined by methane permeate stream divided by methane feed stream times 100. In Fig. 26 the methane loss is plotted versus membrane selectivity for two different pressure ratios.

The figure reveals that the methane loss is smaller at the higher pressure ratio. For the pressure ratio of 80 methane loss starts at 5 % for a selectivity of 100 and drops to

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[1] When looking at the permeabilities in Fig. 25 one has to keep in mind, that the water vapor permeability often strongly depends on its vapor pressure. Most permeability data have been generated near saturation pressure.

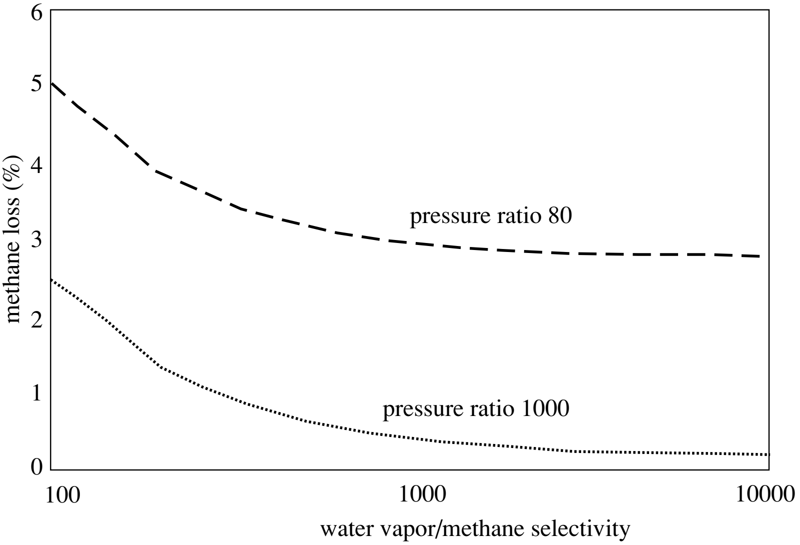

Fig. 26: Methane loss versus selectivity for pressure ratios 80 and 1000, volume fraction of methane in feed 0.2 %.

2,75 % for a selectivity of 5000. But even with a very selective membrane it is never smaller than 2,7 %. At the high pressure ratio of 1000 the methane loss drops to a favorable 0.17 %. However, a pressure ratio of 1000 is quite unrealistic. Additional compression of the feed is out of question. The permeate pressure could be reduced by vacuum pumps; but this idea is not liked by the gas companies because of cost and safety concerns. If a membrane dehydration system is operated at a pressure ratio of 80, the difference between methane loss from a membrane with a selectivity of 500 (3.2 % methane loss) and a membrane with a selectivity of 5000 (2.75 % methane loss) is quite small. Hence, as far as methane loss is concerned there is a small benefit in using the high-selective membrane. The picture changes when the required membrane area is taken into account, which is demonstrated in Fig. 27. Membrane area has been calculated for a feed stream of 1000 m^3 (STP)/h, the water vapor flux through the membrane has been fixed at 1.1 $10^{-2}cm^3/cm^2$ s cmHg. Membrane selectivity was adjusted by variation of methane flux.

As the figure shows, the membrane area required increases strongly with selectivity. There is an 8 x increase of membrane area for a selectivity of 500 and 5000. This example illustrates that it is not always a good strategy to look for the most selective membrane but that a less selective membrane may do a better job.

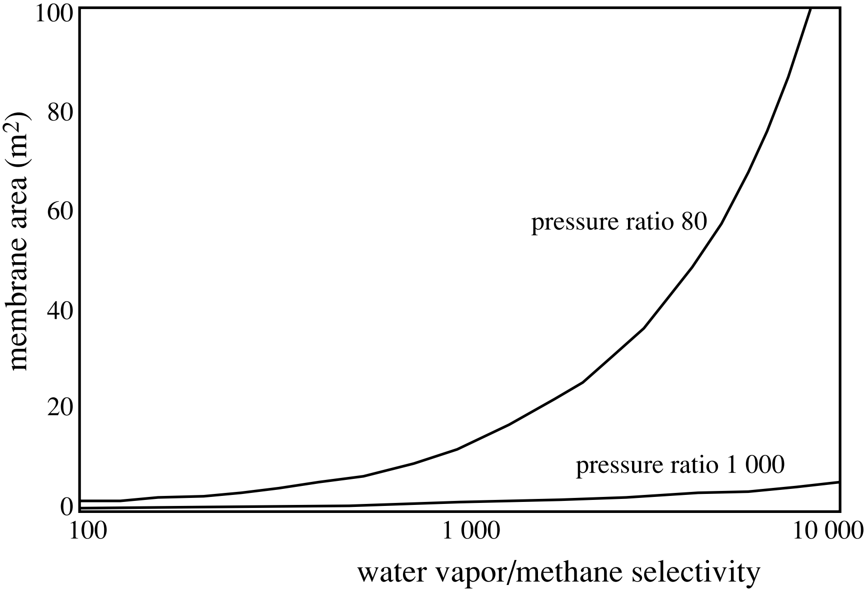

Fig. 27: Membrane area versus selectivity at pressure ratios of 80 and 1000, water vapor flux fixed at 1.1 10^{-2}cm^3/cm^2 s cmHg, water vapor feed concentration 0.2 %, retentate concentration 0.02 %, feed pressure 8 MPa.

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Part II
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1 The Separation of Organic Vapors from Gas Streams by Means of Membranes

K. Ohlrogge and K. Stürken

1.1 Summary

The use of membranes to separate and recover organic vapors from off-gas and process gas streams has grown from an outsider application to an accepted and established technology. At the end of the eighties and the beginning of the nineties the first applications to recover gasoline vapors or solvents were designed and commissioned on an industrial scale.

The membranes, which are used to separate organic vapors, are thin film composite membranes with a rubbery polymer as a permselective layer. The most commonly used membrane type in industrial applications is a flat sheet membrane converted into spirally wound modules [1, 2] or membrane envelopes which have been introduced into the so called GKSS GS membrane module. Gas streams with a high loading of organic vapors are a favoured application. The membrane selectivity of various organic compounds over nitrogen is typically 10 to over 100. A sufficient membrane selectivity, the simple modular design, the ease of operation and advantages in investment and operating costs have led the membrane technology to separate organic vapors. This in turn has led to an established position in the competition concerning adsorption, absorption or only condensation processes.

Membrane separation is applied in off-gas treatment with the goal of recovering organic compounds and separating contaminants in accordance with stipulated clean air regulations. The other main application in production plants is the recovery of valuable compounds from process gas streams, e.g. vinylchloride monomer or propylene. The size of the membrane separation units ranges from some m^3/h to more than 4000 m^3/h. The small scale units are often used to treat the off-gases from dryers or pump exhausts, the big units are installed at gasoline loading facilities to treat the off-gases generated by truck, rail road tanker or ship loading.

Meanwhile approximately 200 membrane units to separate organic vapors have been sold or commissioned. The units have been sold to nearly all industrially developed countries in the world. Approx. 40 % of the units are installed in Germany. This is because of the stringent air pollution regulation. Major developments to introduce this technology have been carried out in the US by MTR, in Europe by GKSS Research Center and its licensees and in Japan by Nitto Denko as membrane producer and NKK as plant manufacturer. Based on the growing success new applications have been developed and are at the threshold of becoming commercial. These new applications include hydrocarbon vapor separation from hydrogen in refineries, hydrocarbon dewpointing of natural gas and the control of the methane number of the fuel gas of gas engines and gas turbines.

1.2 Introduction

Many effluents from processes in the chemical, petrochemical and pharmaceutical industry contain volatile organic compounds (VOCs). In addition to these, VOC emissions are generated by handling, storage and distribution of solvents and gasoline products. The emissions, whose venting into the atmosphere is permitted, are governed by certain governmental regulations. The introduction of new clean air acts at the end of the eighties in Germany [3] and the beginning of 1990 in the US [4, 5] generated a driving force to develop new technologies to meet the new and more stringent emission standards. From the start membrane technology has occupied certain niches in effluent gas treatment. The growing acceptance based on the confirmed performance, reliability and economic efficiency leads to newer and bigger applications for the use of membranes in production processes to recover valuable compounds and to control concentrations in process gas streams. Membrane technology is now, in a wide range of applications, a serious competitor to established technologies like adsorption, absorption or condensation.

1.3 Historical background

Rubbery films play an important rule in exploring and understanding gas permeation through dense films. Publications of J.K. Mitchell [6] in 1831 and Sir Thomas Graham in 1866 focussed on gas absorption in rubbery material and on the first quantitative measurements of gas permeation rates [7]. A very early patent using rubbery membranes to separate different hydrocarbons was filed by Frederik E. Frey from Phillips Petroleum Company. The US Patent 2,159,434 "Process for concentrating hydrocarbons" was granted in 1939. Jean P. Jones filed a second patent on a similar application from Phillips Petroleum titled: "Separation of hydrocarbons from non hydrocarbons by diffusion". This patent was granted in 1952 as US Patent 2,167,493. G.J. van Amerongen [8] and R.M. Barrer [9] have provided very important contributions to the knowledge of the permeation behaviour of polymers. 1981 Roger W. Fenstermaker has filed the US Patent 4,370,150 "Engine performance operating on filed gas engine fuel". This patent describes a membrane separator based on silicone membranes to separate hydrogen sulfide and heavier hydrocarbons from natural gas to upgrade the fuel gas of gas engines. One substantial drawback in the conversion of the available knowledge and the inventions into economic technical feasible operations was the lack of commercially available membranes with acceptable fluxes and selectivities. Activities to develop suitable membranes were started in the eighties in the US, Japan and Germany. The work was pioneered by MTR by evaluating different elastomers as selective layers of thin film flat sheet composite membranes [10]. The favored module configuration was the spirally wound module. Membrane and module development has been performed in cooperation with Nitto Denko. GKSS started processes involving the separation of volatile organic compounds in the middle of the 1980's. Filing process patents associates the developments. Richard Baker, MTR, filed his US Patent 4,553,983 “Process for recovering organic vapors from air” in 1985. This patent is focussed on the treatment of effluents from dryers with a maximum solvent concentration of 2 vol%. Kato et al. from Nippon Kokan Kabushiki Kaisha (NKK) invented, in 1986, a process to separate organic vapors from off-gases using a combination of membrane separation and absorption. The key feature of the GKSS patent “Method for Extracting Organic Compounds from Air/Permanent Gas Mixtures” is the compression of an organic vapor-laden gas stream in order to enhance the recovery of organic vapors by means of condensation or absorption and to optimize the economics of the membrane stage. This patent was filed in February 1988. A process to treat the effluents of a vacuum pump was invented by Gerhard Hauk in 1989 [11]. The vacuum pump was used to supply the feed stream to the membrane module and to provide a vacuum to assist permeation through the membranes. This patent is owned by Sterling-SIHI.

The introduction of industrial plants in the US, in Japan and Germany occured at the end of the eighties. MTR built plants to treat refrigerant vent streams in 1989; NKK commissioned a gasoline vapor recovery unit in 1988 and the first gasoline vapor recovery unit built by the GKSS licensee Aluminium Rheinfelden was commissioned in 1989. Meanwhile more than 180 [12, 13, 14, 15] membrane-based vapor separation units are in operation. For use in the recovery it concludes of all types of common solvents and organic vapors. The customers include the chemical, petrochemical and pharmaceutical industries. A well-explored market is the treatment of gasoline vapor at tank farms and loading facilities for ships, railroad tankers and trucks. A potential market would be emission reduction at petrol stations.

1.4 Membranes for organic vapor separation

1.4.1 Principles

The membranes, which are being used in organic vapor separation, are thin film composite membranes. Typically the membrane consists of a three layer structure: a nonwoven material, e.g. polyester, to provide the mechanical strength, a micro-porous substrate made from polysulfone, polyimide, polyetherimide, polyacrylonitrile or polyvinylidene fluoride and a thin pore-free coating of a rubbery polymer as a selective layer. A common selective coating is polydimethylsiloxane (PDMS) which has a high flux and an adequate selectivity for many organic vapors. Some specific separation problems require higher selectivities as provided by PDMS. In this case the use of a polyoctylmethylsiloxane (POMS) is favorable. This polymer shows higher selectivities but lower permeabilities. The investment costs for the increase in membrane selectivity can be overcompensated by smaller vacuum pumps and compressors.

The advantage of these rubbery membranes besides high flux and acceptable selectivities is the preferential permeability of organic vapors. The preferred permeation of the condensable organic vapors is desirable in order to avoid condensation on the membrane surface.

1.4.2 Selectivity

The crucial parameter for the transport of gas through a dense polymer film is the interaction of the diffusion and the solubility coefficients of the feed gas in the polymer. The diffusion coefficient of a molecule generally decreases with the increase in molecular size. Glassy polymers with stiff polymer backbones act like a molecular sieve. Small gas molecules like hydrogen or helium permeate much faster through the rigid polymer backbone than the bigger molecules of hydrocarbon vapors. An elastomeric polymer acts more like a liquid. The gas transport through an elastomer is determined more by its solubility than by its diffusion coefficient. The high solubility of organic vapors in some elastomers is the reason for their high permeability. This item has been discussed in the chapter "Materials and transport mechanisms in part gas separation with membranes".

The selectivities of various organic vapors over nitrogen of a rubbery thin film composite membrane are shown in Fig. 1.1.

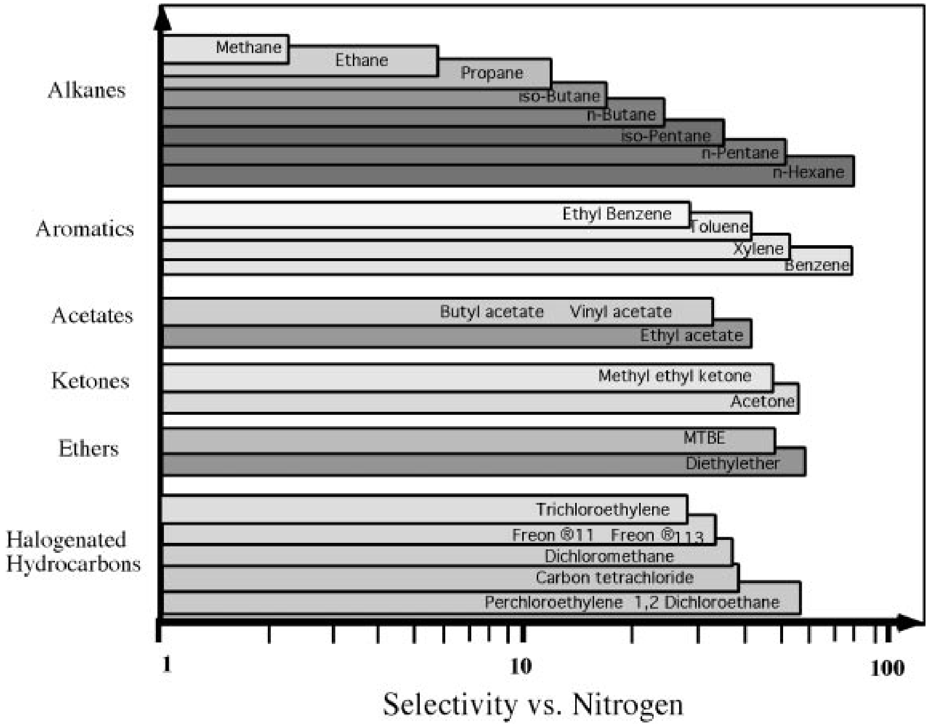

Fig. 1.1: Selectivities of various organic vapors over nitrogen.

The length of the bar shows the highest average selectivity obtained by single gas measurements at ambient temperatures. The selectivity, which can be achieved in a technical process, is dependent on the membrane structure, module configuration and the process parameter. The temperature and the partial pressure of the organic compound have a direct impact on the membrane selectivity.

1.4.3 Temperature and pressure

The permeation of permanent gases increases with the increase in temperature. Because the permeation of organic vapors depends on its solubility, the flux increases with a decrease in temperature. It is advantageous to operate a membrane-based organic vapor separation process in temperatures kept as low as possible in order to achieve the highest possible selectivity. The second important parameter is the concentration of partial pressure of the organic vapor. Whereas the flux of permanent gases through a rubbery membrane is practically independent, the flux of the organic vapor is highly dependent on the vapor pressure. The higher sorption at high organic vapor pressure plasticizes the membrane material and causes an increase of the solvent diffusion coefficient. The flux density dependence of various organic vapors over vapor pressure is shown in Fig. 1.2.

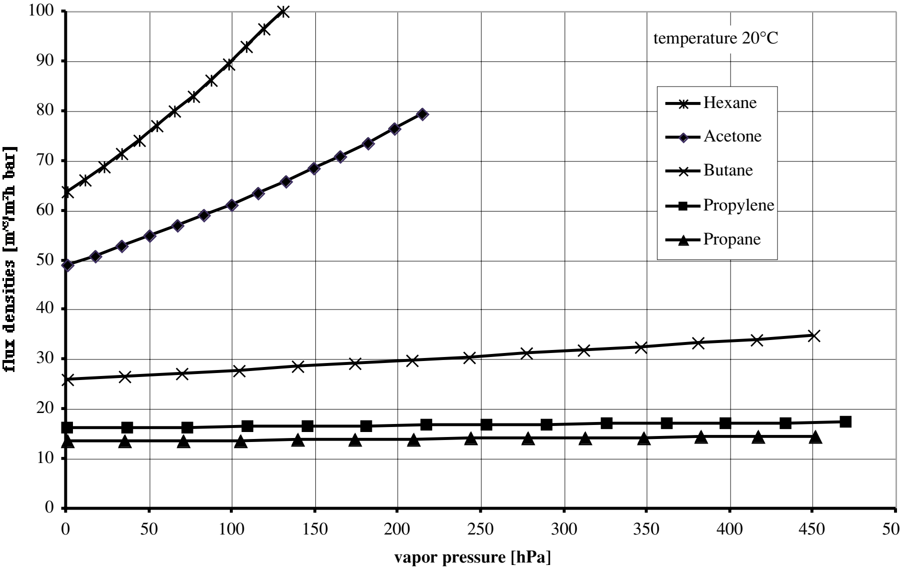

Fig. 1.2: Flux densities of various organic vapors over vapor pressure.

1.4.4 Membrane modules

The membrane modules, which are commonly used in organic vapor separation either spirally wound modules or the envelope type GKSS GS. Capillary or hollow fiber modules are only used in small-scale laboratory applications. The spirally wound module and the envelope module are based on flat sheet membranes. Spiral wound modules are compact and cheaper in comparison to installed membrane areas, but are limited in the mass transfer on both sides of the membrane. The packing density – the ratio of installed membrane area over pressure vessel housing volume – of a spirally wound module varies from approx. 300 to 1000 m^3/m^3 (Fig. 1.3).

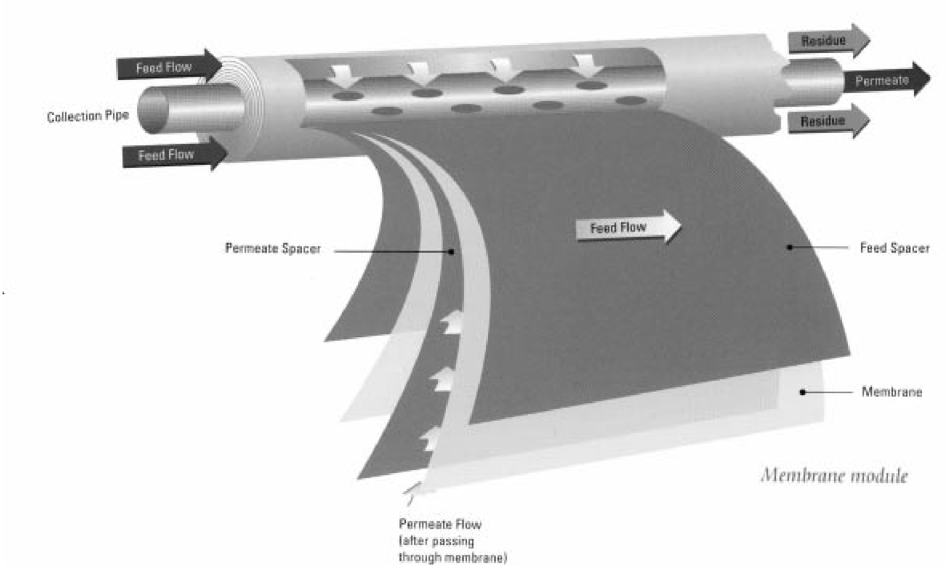

Fig. 1.3: Spiral wound module as manufactured by MTR. Used with permission of MTR.

The envelope type GS module offers advantages in flow distribution and a minimized pressure drop at the permeate side.

The membrane envelope consists of two membranes; fleeces and spacers between the membranes to provide an open space for an unrestrained permeate drainage. Thermal welding at the outer cutting edges seals the membrane sandwich (Fig. 1.4).

The membrane module consists of a pressure vessel, a central permeate tube and a stack of membrane envelopes. The stack of envelopes is divided into asymmetric arranged compartments by means of baffle plates. The design of a compartment is calculated according to an uniform flow velocity over the membrane surface. In correlation to the feed volume reduction caused by permeation the number of envelopes between two baffle plates are reduced. This special design feature allows a design velocity over the

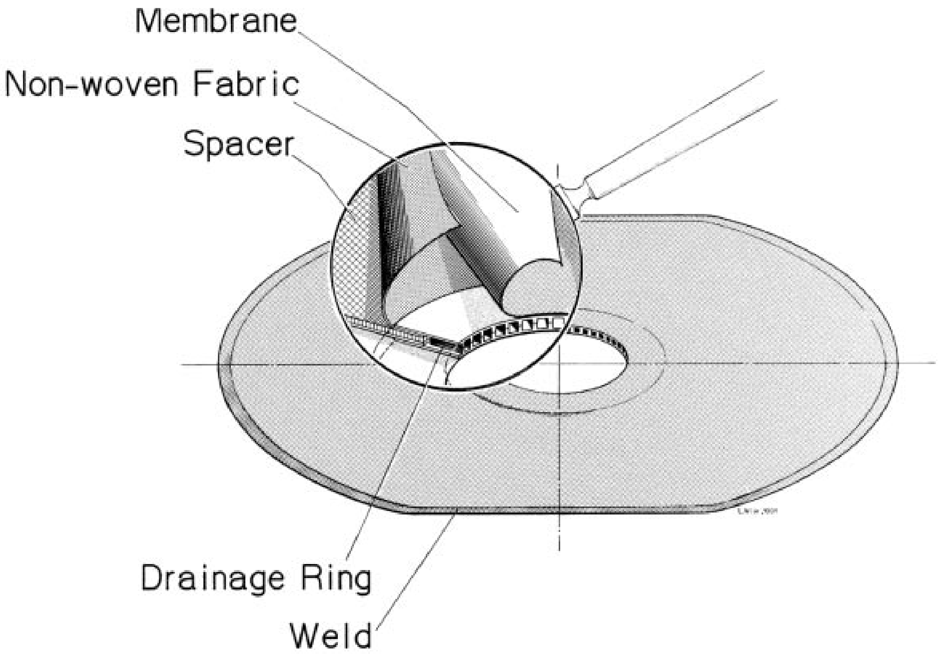

Fig. 1.4: Membrane envelope.

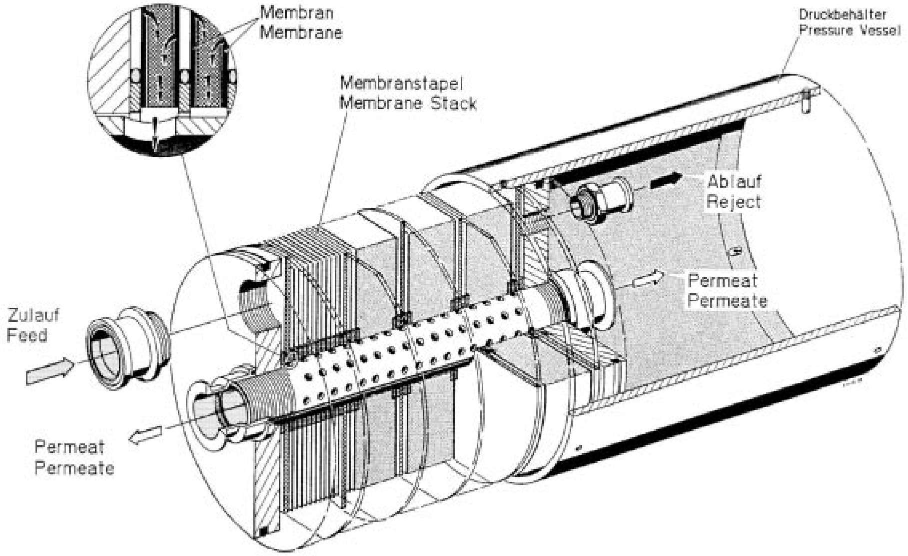

Fig. 1.5: GKSS GS-module.

membrane surface in order to reduce boundary layer effects and to achieve the highest possible membrane selectivity. The packing density variation is dependent on the number of baffle plates from approx. 270 to 450 m^2/m^3 (Fig. 1.5).

1.5 Applications

1.5.1 Design criteria

Most of the organic vapor separation applications are unique and the systems are tailored according to customer or site specific requirements. Fig. 1.6 shows the basic input data, which are necessary to evaluate the membrane separation process. The physical constants of the feed compounds, the operating conditions and the design concentration of the product have to be known in order to calculate the basic lay out. The feed pressure and the degree of saturation of the condensable feed compounds dictate the most effective location of recovery by condensation or absorption. In the case of pressure increase by means of a compressor and a moderate to high organic vapor concentration of the feed, the recovery unit should be placed in front of the membrane stage. If the separation process is operated without feed compression the recovery unit should be placed in the enriched permeate stream at the feed site of the recycle pump. In the case of multi compound streams and very low retentate concentrations the combination of a membrane stage and a post treatment unit could provide the most economic solution.

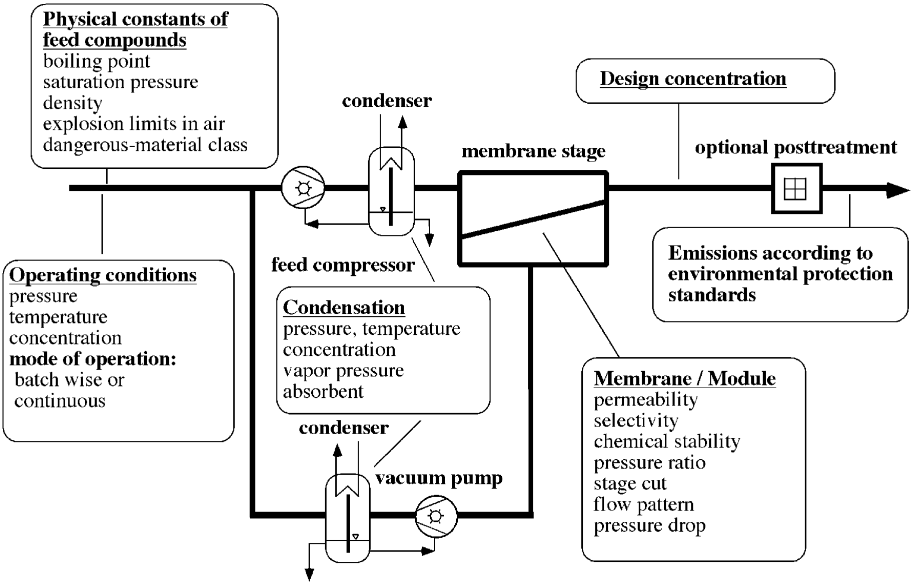

Fig. 1.6: Simplified flow scheme of a membrane separation process.

The polishing of the retentate according to stringent clean-air regulations can be performed by adsorption, absorption, thermal combustion or catalytic conversion.
The design of single stage membrane units depends on the specific application:

- efficient recovery of a valuable product
- achievement of the stipulated clean-air requirements
- a combination of both.

The efficiency of a membrane stage is dependent on:

- intrinsic membrane selectivity
- flow distribution in the membrane module to achieve the highest possible selectivity under operating conditions
- feed pressure
- pressure drop
- pressure ratio (feed pressure over permeate pressure)
- operating temperature.

There is a strong interaction between the demanded retentate concentration and the investment and operating costs of compressors, vacuum pumps and membrane modules. In any case a very low organic vapor concentration of the retentate leads to a high stage cut which requires higher suction capacities of vacuum pumps and compressors.

1.5.2 Off-gas and process gas treatment

Typical applications are the treatment of small volume flows of solvent contaminated off-gas streams in the chemical and pharmaceutical industry. Fig. 1.7 shows the off-gas purification of a stripping column to treat edible vegetable oil. Nitrogen is used to strip the solvent from oil. The off-gas has to be treated according to an outlet concentration < 150 mg hexane/m^3 inert gas.
The process was designed according to the following data:

- Process vacuum and permeate pressure: 30 mbar
- Volume flow: 4 m^3/h inert gas with hexane vapors
- Feed concentration: 300 g/m^3
- Outlet concentration: < 150 mg/m^3
- Service liquid: hexane
- Temperature service liquid: –15 °C
- Recovery rate: 99.95 %

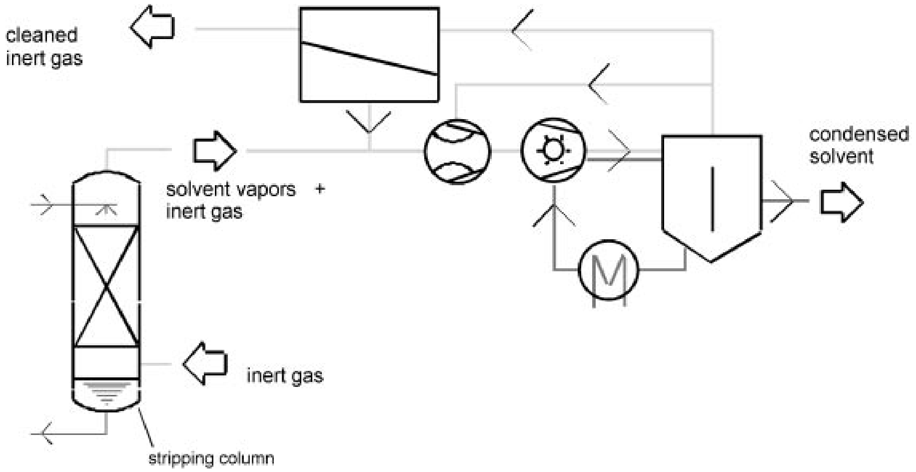

Fig. 1.7: Off-gas purification.

This application shows that it is possible to meet the stringent German TI Air standards with a single stage membrane unit. But this is also an example of the potential for improvement of the process economics. If it is possible to recycle the retentate, the following savings are possible:

- Reduction of stripping gas cost
- Reduction of vacuum pump capacity
- Reduction of required membrane area.

An excellent example for the economic use of membrane technology is the vinyl chloride recovery from off-gases of the PVC production [16]. The vapor pressure of vinyl chloride at 30 °C is 4.51 bar, the residual concentration of a compressed off-gas stream at 5.5 bar is approx. 2 kg/m^3 (STP). Vinyl chloride is a high-value product with a market price of approx. 1,000 DM/t. The common technology to recover the vinyl chloride is multi-stage pressure condensation. The production off-gas is collected in a buffer. It is compressed up to approx. 5.5 bar and the condensation of the vinyl chloride takes place in condensers operated with cooling tower water, the second stage condensation at approx. –10 to –15 °C and the third stage at chilling temperatures of approx. –40 °C (Fig. 1.8). The recovery rate at –40 °C condensation is 92 % and the residual concentration is 0.18 kg/m^3 (STP) (Fig. 1.9).

Vinyl chloride is considered as a carcinogenic solvent and the allowed emission concentration is < 5 mg/m^3. All kinds of recovery units have a post treatment system by adsorption and/or combustion (Fig. 1.8).

The replacement of the second and third condenser by a membrane stage enables a high degree of vinyl chloride separation at condensation temperatures of –70 °C or lower (Fig. 1.10).

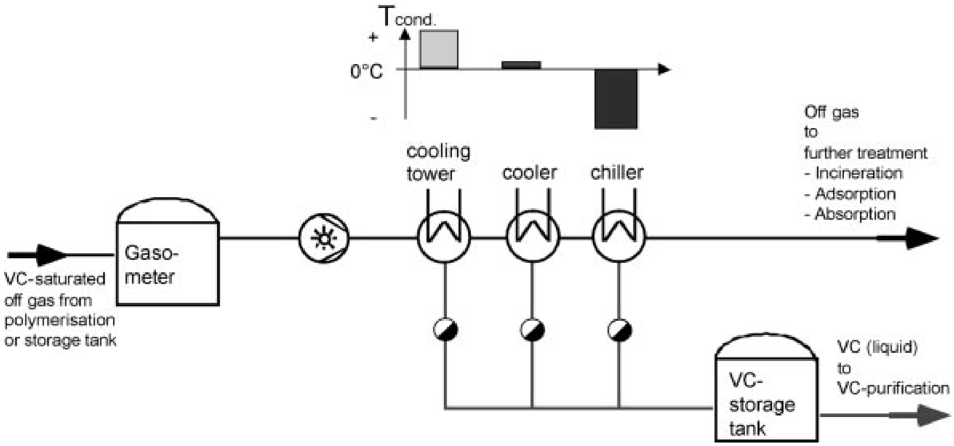

Fig. 1.8: Conventional vinyl chloride recovery.

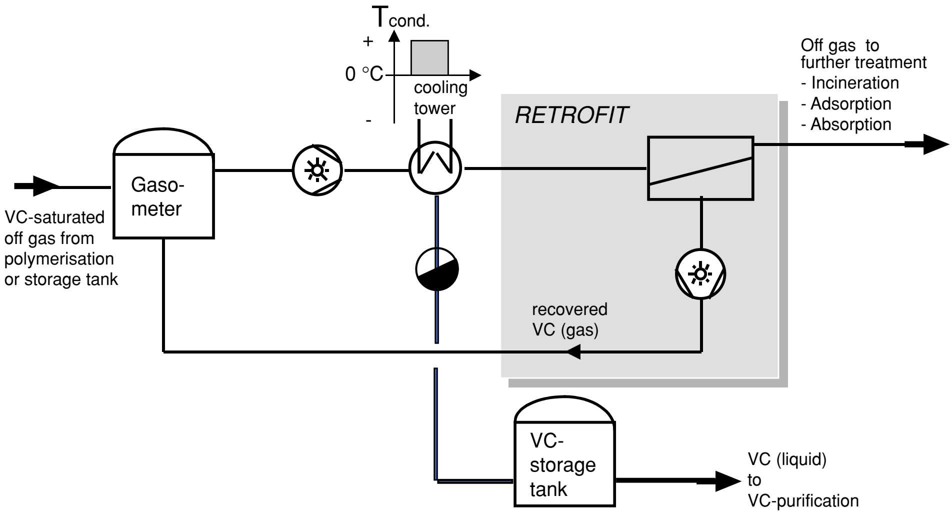

Fig. 1.9: Retrofit of multi-stage condensation unit.

Another advantage of using membranes is that it enables a continuous operation without defreezing the condenser surfaces in case of presence of water vapor in the off-gas.

1.5.2.1 Gasoline vapor recovery

The principle of emission reduction in the chain of gasoline distribution is vapor balancing. The volume of vapor, which is displaced when a volume of liquid is filled into a

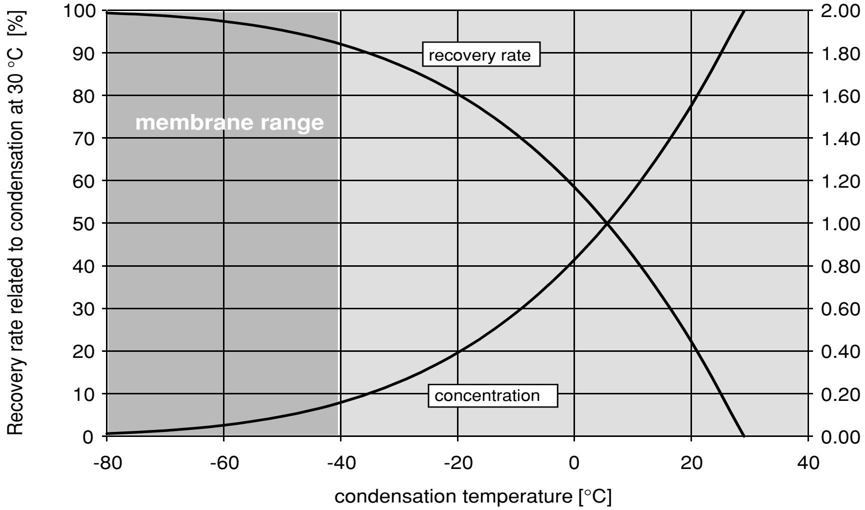

Fig. 1.10: PVC production: Recovery rate and outlet concentration vs. condensation temperature.

tank, is collected and returned to a tank from which a liquid is drawn off. But it is expected that a surplus of volume will be created during filling and transfer procedures. This is because of the possible change of temperatures and pressures as well as evaporation generated by turbulences of the liquid phase during filling procedures. The average gasoline vapor concentration in off-gases is approx. 20 to 40 vol%, which corresponds to approx. 600 to 1200 g hydrocarbon/m^3 air. The allowed vent-gas concentration is governed by established clean-air regulations. The European stage II directive 94/63/EC allows 35 g HC/m^3 air, whereas the German TI-Air is restricted to 150 mg/m^3, a value which is approx. 230 times lower.

In case of gasoline vapor-loaded off-gases the recovery of the organic vapors is favored over destruction.

Commonly used recovery techniques are:

- Adsorption
- Absorption
- Condensation
- Membrane separation.

In order to achieve high recovery rates and low investment and operating costs the combination of different recovery techniques have been realized.

A membrane-based gasoline vapor recovery unit designed to meet the stringent TI-Air standards consists typically of:

- a recovery stage by absorption
- a membrane separation stage and

- a post treatment by means of a pressure swing adsorption unit or a gas motor where the retentate of the membrane stage is used as a fuel gas to supply the combustion engine (Fig. 1.11).

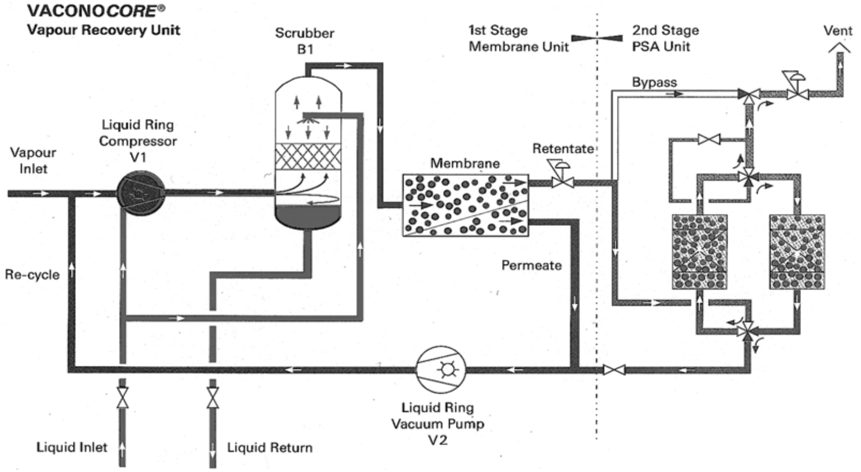

Fig. 1.11: Gasoline vapor recovery system used with permission of Aluminium Rheinfelden

The inlet vapor coming from a gasholder to balance volume peaks or coming directly from the loading facility is fed to a feed compressor. The recovery takes place in a scrubber. The system utilizes lean liquid product as a service liquid for the liquid ring compressor and as scrubbing fluid for the recovery unit. The recovered product is absorbed by the scrubbing action and returned to storage as an enriched stream. The gas flow leaves the top of the scrubber with a residual concentration in accordance with temperature and pressure and is introduced into the membrane stage. The hydrocarbon selective membrane separates the stream into a lean retentate stream and an enriched permeate stream. A vacuum is applied at the permeate side to support the permeation process. The permeate is recycled and mixed with the inlet vapor at the suction side of the feed compressor.

The retentate contains a residual organic vapor content, which consists mostly of light hydrocarbons. The stream is introduced into the integrated pressure swing adsorption unit (PSA). The unit consists of adsorption beds arranged parallel and a service of control valves. The control valves are cycled in a pre-determined sequence. This allows the operation of one bed whilst the other bed is regenerating and provides a continuos process. Part of the clean vent stream is by-passed and recycled to be used as a purge gas stream for regeneration. The pressure of the membrane process is used for an enhanced adsorption whereas the regeneration is supported by the vacuum of the membrane process. The purge gas stream is returned and mixed with the inlet gas.

In case of gasoline-tank farm applications in Germany membrane-based recovery plants have the highest market share more than 55 %. The hybrid process of membrane technology combined with pressure swing adsorption was the best-selling system in the case of TI-Air requirements.

In the case of gasoline vapor recovery two types of membranes are used. The PDMS (polydimethylsiloxane) membrane and the POMS (polyoctylmethylsiloxane) membrane.

The PDMS membrane is a membrane which is characterized by high flux densities and moderate hydrocarbon over air selectivities, whereas the POMS membrane has a higher selectivity and moderate gas fluxes.

The intake concentration of a unit treating the off-gases from a tank farm varies from approx. 600 to 1200 g/m^3. The variation is caused by the vapor pressure of the gasoline (e.g. summer or winter quality), temperature and loading procedure (e.g. top loading or bottom loading).

A case study compares the use of PDMS and POMS membranes for any given design criteria.

Capacity of feed compressor:	1000 m^3/h	
Feed pressure:	3.5 bar	
Permeate pressure:	150 mbar	
Feed concentration:	20 vol% HC	
Absorption medium:	lean gasoline	
Temperature:	25 °C	
Isothermal compressor efficiency:	0.38	
Isothermal vacuum pump efficiency:	0.30	
Inlet concentration PSA:	10 g/m^3	
PSA purge gas ratio of retentate volume flow:	15	
Vent gas purity:	150 mg/m^3 (TI Air requirement)	= 99.99 % recovery rate
	10 g/m^3	= 98.3 % recovery rate
	20 g/m^3	= 96.7 % recovery rate
	35 g/m^3 (EU stage1 requirement)	= 94.2 % recovery rate

Feed gas composition:	Methane:	0.017 vol%	Ethane:	0.049 vol%
	Propane:	0.642 vol%	i-Butane:	3.581 vol%
	n-Butane:	7.592 vol%	i-Pentane:	4.117 vol%
	n-Pentane:	2.275 vol%	Hexane:	1.323 vol%
	Heptane:	0.220 vol%	Benzene:	0.183 vol%
	Nitrogen:	63.280 vol%	Oxygen:	16.720 vol%

	PDMS	POMS
	Retentate concentration [g/m^3]	
	0.15 (TI Air)	
VRU capacity [m^3(STP)/h]	524	611
Membrane area [m^2]	60	186
Stage cut [%]	53.2	44.3
Specific energy consumption [kWh/m^3(STP)]	0.334	0.262
	10 g/m^3	
	612	709
	58	178
	44.2	33.9
	0.261	0.201
	20 g/m^3	
	663	745
	47	139
	38.8	30
	0.227	0.183
	35 g/m^3 (European stage I Ordinance)	
	705	775
	38.2	108.5
	34.3	26.6
	0.203	0.169

It is clearly shown that “slower” membranes require approx. 3 times more membrane area to achieve the same vent gas purity. The higher selectivity, on the other hand, causes a reduction of the stage cut, which leads to a reduced recycled permeate stream.

The suction volume of the compressor consists of the flow from the loading terminal and the recycled permeate flow. The reduced stage cut effects the relation between the flows share of both and causes an increase of VRU capacity, which is in direct relation to the specific energy consumption. The second influence on the stage cut is the required vent gas purity. Any increase of the allowed hydrocarbon concentration in the vent gas leads to a decrease of the stage cut.

In summary: Retentate concentration and membrane selectivity have a direct influence on the stage cut. The membrane permeability has an effect on the required membrane area. Investment costs for compressor, vacuum pump and membrane area have to be balanced with the operating costs. As a result of the stringent clean-air requirements the POMS membrane was the first choice of all realized plants.

Retrofitting of adsorption units

Old vapor recovery units often do not meet the new and more stringent clean air requirements. One possibility of retrofitting of an adsorption unit is the installation of a membrane unit in the feed line before the entrance into the adsorption unit. The membrane stage could be used to shave the peaks at fluctuating hydrocarbon concentrations and to reduce the amount of higher hydrocarbons. Figure 1.12 shows a simplified flow scheme of retrofitting an adsorption unit by means of the installation of a membrane stage.

Table 1.1 shows the effect of three steps to toughen up a vapor recovery unit to meet the new TI Air standards and to operate the unit at the highest efficiency.

It is confirmed by realized installations, that it is possible to retrofit existing plants with acceptable investment costs to meet new clean air standards and to enhance the plant capacity.

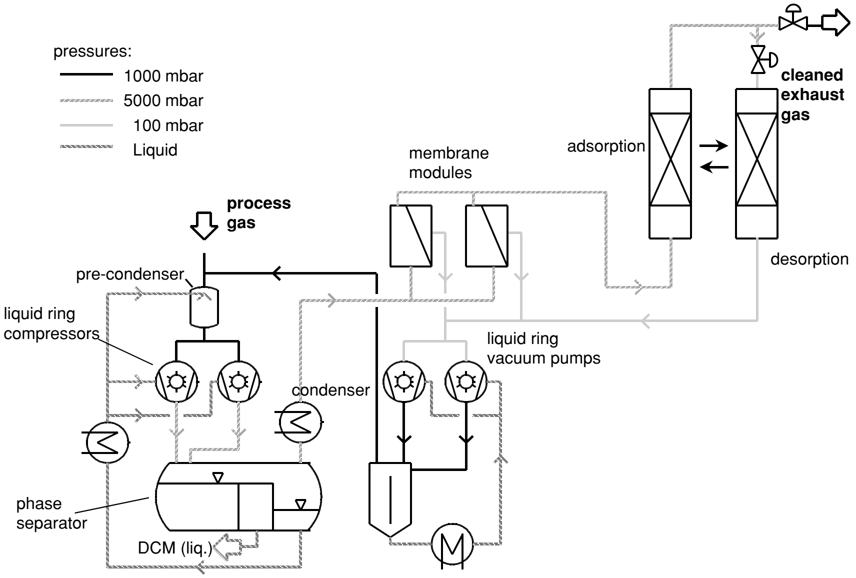

Fig. 1.12: Retrofitting of an adsorption unit to meet TI Air standards.

Tab. 1.1

Starting conditions	1 Retrofitting Enhancement of vacuum pump capacity	2 Retrofitting Installation of a membrane stage	3 Retrofitting Enhancement of blower capacity
Emissions > 3kg/h	3kg/h	<150 mg/m^3 goal 20 mg/m^3 actual	<150 mg/m^3 goal 70 mg/m^3 actual
Electrical power 64.5 kW installed	94.5	131.5	131.5
Electrical power 57 kW actual	86	118	120
VRU capacity 280m3/h	280	280	350
Specific power Requirement 0.2 kW/h	0.31	0.42	0.34

1.5.2.2 Polyolefin production processes

The potential use of membrane separation in polyolefin production processes will be in the areas of raw material purification, chemical reaction and product purification and finishing [17, 18, 19]. Hydrocarbon vapors including propylene and ethylene can be separated and recovered from nitrogen and light gases such as the methane and hydrogen in polyolefin production vent streams. On the other hand, nitrogen can be purified to be re-used as a purge gas (Fig. 1.13).

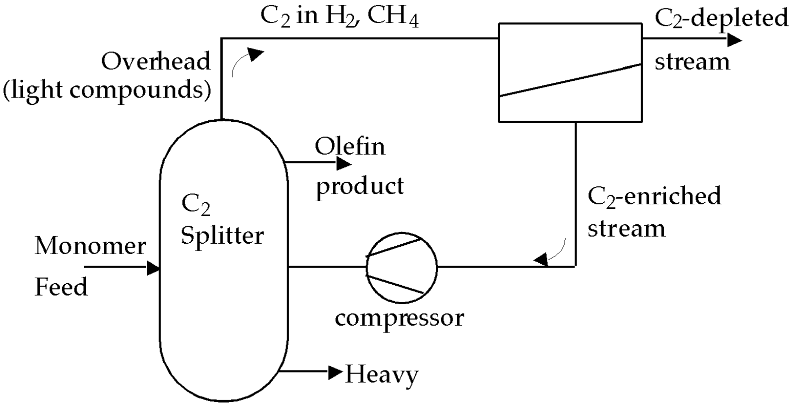

Fig. 1.13: Column overhead recovery.

In order to meet quality requirements the raw material has to be purified. In the case of independently separated isolated plants the purification takes place in a splitter column. The build up of nitrogen and light gases has to be removed from the overhead of the splitter column. Because of the significant amount of unreacted monomers, which represents a high commercial value, the separation of the organic compounds offers the opportunity to reduce production costs. The operation of the membrane process is supported by the available pressure of the overhead column. The monomer-depleted residual stream of the membrane stage, which contains nitrogen, hydrogen and methane is either fed for further treatment to a flare or used as fuel. The monomer-enriched stream is recompressed and recycled to the splitter. The olefin polymerization takes place in presence of the monomer plus catalyst, various co-monomers, solvents and stabilizers, which are contacted at high pressure in a polymerization reactor. The polymerization reaction is performed in the gas phase or in a slurry phase. Butane or hexane are used as organic solvents. The raw polymer product has to be treated because of the amount of unreacted sorbed monomer, co-monomers and processing solvents. The resin is introduced into a purge bin where nitrogen is used to remove and absorbed monomer or process solvents. The composition of the vent stream leaving the purge bin depends on the degree of polymer purifying, the polymer product and the kind of polymerization process. The typical membrane-based monomer recovery process consists of compression of the purge bin vent stream, low temperature condensation and residual monomer separation by means of selective membranes. The vent stream can be purified up to 9.9 % nitrogen in case the stream is recycled to the purge bin. High nitrogen purity requires an increase in membrane area and compressor capacity because of the increased stage cut which leads to lower permeate concentration and higher permeate volume (Fig. 1.14).

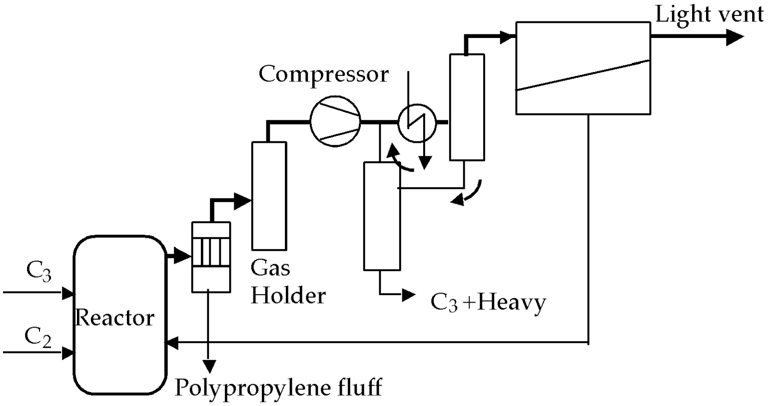

Fig. 1.14: Membrane based monomer recovery by means of compression and condensation.

1.6 Applications at the threshold of commercialisation

1.6.1 Emission control at petrol stations

A spin-off of the activities of gasoline vapor recovery at gasoline tank farms is the development of a system to reduce emissions generated by the operation of petrol stations. In the case of car refuling, the connection between the dispenser nozzle, the petro-tank filler pipe is the only area open to the atmosphere. To reduce emissions during refueling vacuum assisted vapor return systems have been introduced in many countries. In order to avoid the emission transfer from the tank filling point of the car to the vent pipes of the storage tanks an air over liquid ratio of 1:1 of the vapor return system has been stipulated. An investigation of the TÜV Rheinland has shown that the efficiency of catching emissions by means of the 1:1 vapor return ratio is limited to an average of approx. 75 % [20]. The difference between a minimum value of 50 % and a maximum value of 90 % in vapor return is caused by differences in the construction of car filling pipes. In order to enhance to vapor return rates a surplus of air-/vapor volume has to be returned. Tests have shown that the increase of the air over liquid ratio to 1.5:1 leads to an improvement of the efficiency of between 95 to 99 %, depending on the type of car

[21]. The enhancement of the vapor return rate is only possible if no additional emissions are generated. A membrane-based vapor separation system to treat the breather pipe vent gases of storage tanks enables emission reduction during car refueling without creating any additional emissions. The essential requirement is a leakage proof installation of tanks, pipes and dispensers. Furthermore, the installation of over-/under pressure safety valves at breather pipes and check valves at the filling and vapor-balancing couplings of the storage tanks. Because of the surplus of returned vapor volume a pressure build-up occurs in the storage tanks. At a given set point of a pressure gauge, which measures the differential pressure between tank pressure and atmospheric pressure, e.g. 6 mbar, the vacuum pump of a membrane separation system is activated. This system is installed parallel to the vent stack of the storage tanks. A pneumatic valve in the retentate line of the membrane module is opened by the applied vacuum. The overpressure of the storage tanks causes a volume flow, which is released by passing the membrane stack. The gasoline vapors are separated from the off-gas and clean air enters to the atmosphere. After the lower set point of the pressure gauge, e.g. 3 mbar, is reached, the system is deactivated (Fig. 1.15).

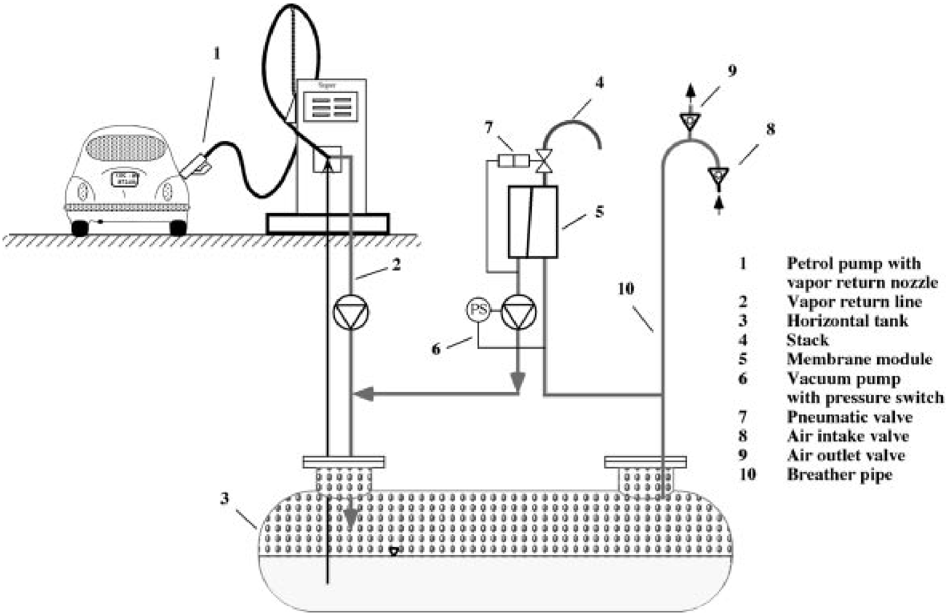

Fig. 1.15: System to reduce emission at petrol stations.

Besides the advantage of emission reduction the wet stock losses of gasoline storage can be reduced because diffusive emissions are avoided and most of the generated gasoline vapor is returned to the storage tank. Because of the simplicity and the nearly maintenance-free operation the system is particularly suitable for petrol station applications.

1.6.2 Natural gas treatment

Natural gas produced at the well head has to be treated in several processing steps especially dehydration and hydrocarbon dew pointing in order to meet the required pipeline and quality specifications. Water and higher hydrocarbon have to be removed in order to avoid the build-up of gas hydrates. The commonly used state of the art processes, such as absorption and cryogenic condensation, have shortcomings with respect to environmental aspects, energy consumption, weight and space requirements. A reliable and proven membrane process could offer a serious alternative to established techniques.

Basic process data concerning the development of organic vapor separation are available. The real challenge is the transformation of the available knowledge into high-pressure applications. Several drawbacks such as the compaction of the substructure of composite membranes and the influence of the boundary layer on the membrane selectivity have to be overcome. Pore structure and polymer compositions have to be suited to the high operating pressure in presence of higher hydrocarbons [22, 23].

Test plants to evaluate membrane performance and process options have been commissioned. Potential first applications include the treatment of smaller natural gas streams. Hydrocarbon dew pointing and fuel gas conditioning for gas engines and turbines are very similar in terms of the basic engineering. A combustion engine needs a certain fuel gas specification, which is defined by the methane number. Higher hydrocarbons have a severe impact on the anti-knocking property. In many cases gas associated with oil production is flared. The need for a self-sufficient energy supply or up-coming environmental regulations lead to the use of this associated gas as fuel gas. The composition of this gas is often highly dependent on the ambient temperature of the oil well. During hot summers an increase of higher hydrocarbons occur due to evaporation which causes an unstable operation of the gas engine. Membrane separation offers a simple technique to remove the higher hydrocarbons and so increase the methane number to a suitable value. The technology has been proven by pilot tests. The methane number has been enhanced from approx. 35 to the target of higher than 50 under the given site-specific conditions.

Some chemical production processes use the municipal gas supply as chemical feed stock. In some cases the gas has to be treated to meet the production specifications. Pressure swing adsorption is often used to remove higher hydrocarbons. Drawbacks of this application are the limited lifetime of the adsorber in the presence of higher hydrocarbons and the costs for replacement and transportation of the used adsorber material. The separation of higher hydrocarbons by means of membranes provides a simple and reliable solution to overcome the drawbacks. Two design options can be offered:

- recycling of the permeate and re-mixing with the gas supply
- the use of the permeate as boiler fuel.

In the case of recycling no methane losses occur but the permeate has to be recompressed and a condensation unit has to be installed to separate the higher hydrocarbon

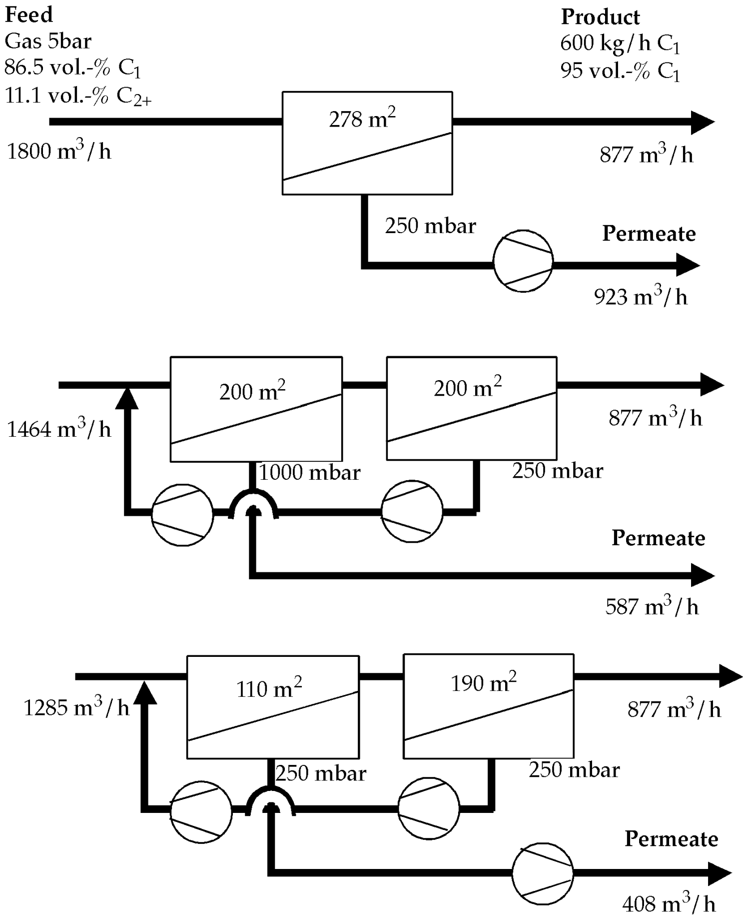

Fig. 1.16: Options to treat municipal gas according to chemical production specifications.

from the enriched permeate stream. The realized system consists of a membrane stage and the permeate was used as boiler fuel (Fig. 1.16).

1.6.3 Hydrogen/Hydrocarbon separation

Process and off-gas streams in refineries and the petrochemical industry often contain hydrogen and hydrocarbons. The hydrogen stream has to be purified before it can be reused. Large volume streams are treated by cryogenic condensation and fractional distillation and in the case of smaller streams by pressure swing adsorption. Elastomeric membranes have certain hydrogen/hydrocarbon selectivities. The increase of selectivity is, in terms of hierarchy, similar to the depiction in Fig. 1.1 "Selectivities of various organic vapors over nitrogen". The real value is lower because of the higher permeation rate of hydrogen in comparison to nitrogen. Hydrogen selective membranes, which are based on glassy polymers, are often sensitive with regard to condensed hydrocarbon. Condensation on the membrane surface can occur if the feed stream is depleted from nitrogen and the hydrocarbon dew point is achieved. Liquid hydrocarbons can cause unwanted swelling or destruction of the glassy membranes. The combination of a membrane separation stage consisting of anorganophilic elastomeric membrane as the pretreatment step and a hydrogen selective membrane based on a glassy polymer offers a technology to treat small or moderate volume flows. If very high purities are required a posttreatment system, e.g. pressure swing adsorption, can be combined with the membrane stage.

1.7 Conclusions and outlook

The separation of organic vapors by means of membranes is, as yet, a niche application. The growing acceptance brought above by references proving performance and reliability supports the growth of market share. Environmental regulations encourage recovery techniques rather than destruction. Membrane technology provides the opportunity to enhance the recovery conditions by means of condensation or absorption. Condensable compounds can be separated from non-condensable compounds. The simplicity of the process, the ease of operation, the long lifetime of membranes and investment and operating costs are demonstrated. The experience of more than 10 years leads to a higher degree of knowledge, popularity and confidence in the technology. End-of-pipe installations have at present the higher market share. This trend will presumably switch in the future to process integrated membrane systems. If the use of membranes for hydrocarbon dew pointing of natural gas is accepted by natural gas producers, the technology will become a push concerning dissemination and total amount of produced membrane area.

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2 Gas Separation Membrane Applications

D. J. Stookey

2.1 Introduction

The previous chapter outlined the phenomena and theory associated with gas separation membranes. The fundamentals of mass transfer and the process design equations that model membranes were also addressed. In this chapter, our attention turns to the industrial application of gas separation membranes, specifically separations with polymeric membranes.

Gas permeation is a scale independent phenomenon. Thus, it is not surprising that membranes applications are represented over a very wide range of membrane sizes. The smaller sizes are typically found in laboratories, but gas separation membranes are now finding utility in commercial analytical products and instruments. One of the smallest is the square millimeter scale membranes incorporated in electronic chips by I-Stat for blood gas assays [1]. This chapter however will focus on applications where the gases separated have commercial value and industrial utility. Presently typical membrane installations of these types range in size from one to 10,000 square meters. However, the range is ever increasing as membrane technology gains ever-wider acceptance. Proposals for membrane systems approaching the square kilometer (one million square meters) scale are now under study for gases-to-liquids projects [2, 3]. It is fair to say that gas separation membranes have become an accepted technology.

There exists a variety of applications for which gas separation membranes have been applied along with their commercial membrane suppliers. The process engineer facing the task of designing a gas separation process is well advised to consult with these suppliers to assist in his design. If the task involves common gas species, it is highly probable that the application has already been commercialized or is under consideration. This chapter provides an overview of some of these commercial applications. Also provided is an overview of considerations, limitations, and hurtles to commercialization of new applications for gas separation membranes. Development of a new membrane for a new application is not for the faint of heart.

Each successful application of gas separation membranes is the result of a whole series of successful technical and commercial activities. Steps included in this series includes the following:

1. Membrane material selection – Does a material exist with suitable permeability and selectivity to separate the components involved?

2. Membrane form – Can the membrane material selected be formed or applied into a film or hollow fiber form suited to the application?
3. Membrane module geometry – Can the membrane formed be incorporated into a module geometry that accommodates conduits for feed and product gases, optimum driving force for the separation, efficient membrane area density, and with minimal pressure head loss (energy)?
4. Compatible sealing materials – Are sealing and tubesheet materials available that are compatible with the gases and process streams involved in the intended application and with the module manufacturing process?
5. Module manufacture – Can a reliable membrane module be manufactured in a cost effective manner?
6. Pilot or field demonstration – Will the membrane module perform to expectations in the intended environment?
7. Process design – Can the membrane module be incorporated into a flowsheet with suitable controls and safeguards for optimal operation and accommodate non-routine events such as start-up and shut-down?
8. Membrane System – Can the membrane assembly be packaged into a deliverable system that will operate in concert with peripheral equipment in the intended environment?
9. Beta Site – Can a customer or partner be identified who will accept the risks associated with new technology and initial installation at a meaningful and acceptable scale of operation?
10. Cost/Performance – Does the membrane application perform against alternatives and meet competitive challenges?

2.2 Membrane application development

2.2.1 Membrane selection

The selection of materials for gas separation membranes requires the matching of performance characteristics of the materials available with the application. Much of the selection process has historically been a trial and error process involving many of the steps in the series outlined above. Not surprising, the selection process is typically guided by a team of polymer chemists and physicists having insights into polymer mechanics and physics. It is not within the scope of this article to describe this selection process, but rather to provide an overview of some of the key elements and considerations.

The gas separation characteristics have been measured and reported for the common gases for many polymers. Indeed, in the preceding chapter, materials have been identified and commercialized by membrane suppliers for many of the common separations. Having identified a gas separation of interest, a thorough review of the available literature is in order. This must include patent literature as many researchers have sought protection for membranes formed of proprietary polymers and their application in many specific gas separations if not for membrane separations or devices as a whole.

The gas permeabilities for some common polymers used in gas separation membranes are reported in the preceeding chapter. Fig. 2.1 shows the relative flux rates for a variety of gases for a polyetherimide film.

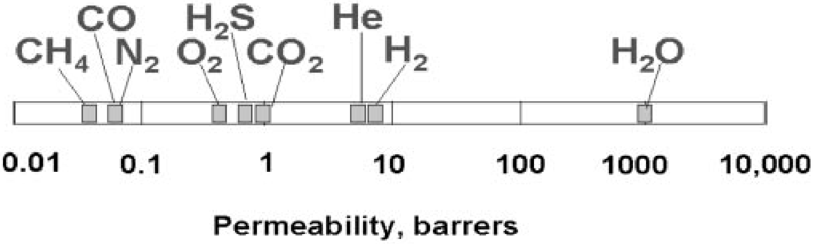

Fig. 2.1: Permeability of common gases through a polyetherimide film.

Inspection of this diagram shows that gas permeability is not determined by the size of the gas molecule. One immediately sees a wide, nearly six-decade, range in transport rates of different gases. Notice also that the permeability of helium, the smallest molecule, is slower than the larger hydrogen and much slower than water in this polymer. Similarly, carbon monoxide transports much slower than its larger cousin, carbon dioxide does. Furthermore, the relative fluxes vary between different polymers. Thus, it can be seen that the researcher must be largely guided by intuition and statistical analysis of data to guide his selection.

The membrane thickness, the application temperature, and other species present further complicate the selection of a membrane polymer for a specific gas separation. Equations show that the gas fluxes through the membrane are inversely proportional to the membrane thickness, l. Most of the published gas permeability data arises from pure gas measurements on flat, thick, dense films supported on a porous backing medium to accommodate the applied pressure differential. Thus while a specific polymer may be chosen for its favorable selectivity, it may very well be impractical if it cannot be fabricated into a very thin membrane separating layer that is stable in the intended application.

Permeability and selectivity, the relative permeabilities of the species being separated from a mixture, are very strongly influenced by the membrane's operating temperature [4, 5]. This arises from the dependence of permeation in polymers on the solubility and diffusivity of gases in the polymer. Permeability, P_i, is typically correlated with absolute temperature, T, by the empirical relationship

$$P_i = K_i \exp(-E_i / RT) \qquad (1)$$

where K_i and E_i are empirical correlation coefficients determined from laboratory and field test data. K_i and E_i *a*re unique to each gas specie and can differ greatly between gases and polymers. The membrane selectivity, α_{ij}, for a gas pair *i-j* is given by the relationship

$$\alpha_{i,j} = P_i / P_j = (K_i / K_j)\exp(-(E_i - E_j)/RT) \qquad (2)$$

Thus, it can be seen that the membrane researcher must consider operating temperature in making his recommendation for the membrane material.

The presence of condensible, polar, and associating components in the mixture being processed can also influence the permeabilities and selectivities of gas species being separated. Polymer free volume, the free space between polymer molecules, plays a major role in permeation of gases through membranes [6, 7].In addition to forming sub-micron membrane thicknesses, membrane chemists have employed a variety of techniques for increasing the free volume locked within the membrane skin during its formation [8, 9]. Others have sought to alter the free volume and modify the surface by various chemical treatments [10, 11]. In altering the polymer free volume in the membrane skin, variations in transport rate and selectivity can be accomplished. Sorption of components in the mixture being separated within the free volume and on the membrane surface can substantially alter gas permeabilities. The sorbed species effectively occupy space and hinder the passage of other components. This phenomenon is employed in many vapor recovery membranes discussed elsewhere in this book. Sorption can be so complete as to block the transport of otherwise highly permeable species [12, 13]. An example is the separation of hydrogen from hydrocarbons with PTMSP. Auvil and others have shown that the free volume in PTMSP can under proper conditions so completely fill with sorbed and condensed heavy species such as hydrocarbons as to render the membrane nearly impermeable to light species such as helium or hydrogen [14]. To the extent that all polymers have some free volume, sorption and free volume filling can become a factor in performance of all membranes and in the selection of the polymer for the gas separation membrane.

Commercial membrane suppliers have each selected and developed membranes with these factors plus a host of other considerations in mind, usually with a specific target application in mind. Sizeable investments in development and manufacturing capital are now in place. Thus as new gas separation applications surface, membrane manufacturers first screen the separation on available products. Frequently the new separation if fitted to the available products rather than the product to the application. Polymers more suited to the separation in terms of selectivity may indeed exist, however the choices may be restricted to less than optimum performance due to economics and availability. Some manufacturers are developing composite structures as a means for increasing the flexibility and choice of polymers employed in the separation. This is discussed in more detail in the next section.

2.2.2 Membrane form

The trans-membrane flux is inversely proportional to the membrane thickness and is directly proportional to the membrane area and to the applied pressure differential across the membrane. Thus, a membrane manufacturer's primary objectives typically revolve around means for producing the thinnest possible membrane in a structural form that will accommodate the applied pressure while maximizing the membrane surface area. Thus, knowledge of the structural and mechanical properties of the membrane material is of paramount importance. Unfortunately, many polymers of interest as gas permeable membranes are rubbery materials with poor mechanical strength. Hence, many membranes require an underlying support material that can accommodate the applied pressure load.

Membrane properties, as discussed in the previous section are typically measured in dense polymer film approaching one millimeter in thickness, less than 100 cm^2 area, and supported on a porous ceramic or metal backing plate. Scale up of flat film membranes to commercial scale has been quite limited, typically to applications involving small quantities of gas, low-pressure differentials, and to high flux, low selectivity membranes.

Other flat film membrane designs employ textiles, non-woven fabrics, or porous polymeric sheets as backing material to the membrane film. Composite membranes of this construction enable the separating layer thickness to be reduced to a few microns. When high flux polymers are employed, the transport resistance of the non-selective support layer can become a significant resistance. The effect of resistances in series with the separating layer resistance has the effect of reducing the overall membrane selectivity [15]. Hence, much attention is given to minimizing the supporting layer's resistance.

A number of researchers have produced capillary tubing and hollow fibers from materials of sufficient strength to avoid the need for a porous support. These materials are typically melt spun into hair size fibers having dense walls of sufficient strength to obviate the need for a supporting layer.. While the dense layer offers substantial resistance and limits the permeation flux, the hair-size of the hollow fibers enables designs that accommodate high membrane surface area densities (area per unit volume) [32].

Loeb and Sourirajan [16] introduced the unitary asymmetric membrane. These membranes consist of a microscopically thin skin on a porous support formed of the same material as the skin. By judicious selection of solvents, coagulants, and processing conditions, these researchers were able to precipitate polymer solutions to form both skin and porous support in a single processing step. The asymmetric membrane is known to produce the thinnest of membranes. Kesting, et al., [17] have shown membrane thicknesses below 50 nanometers (500 Angstroms) are possible in the unitary asymmetric membrane. Unitary asymmetric membranes are formed in both flat sheet and hollow fiber forms. Polymers selected for the asymmetric form must obviously be of sufficient strength to perform the role of the porous support while also serving as the separating medium. Unitary asymmetric hollow fibers are produced with collapse pressures in excess of 100 atmospheres. In this case, the economics of the membrane product is controlled by the availability of low cost polymers that also have permselective properties. The unitary asymmetric membranes are thus limited to selections from the cellulose acetate, polysulfone, polycarbonate, and polyimide families.

Many polymers have been tailored for specific permselective properties, unfortunately often not without penalty. Many of these materials have poor mechanical properties or are costly due to the exotic materials involved or their relatively small production volumes. Many researchers pursue composite membrane forms as a means of overcoming these limitations. These involve creating a composite thin film or an asymmetric layer of the desired separating material on a porous support [18, 19]. While this is a seemingly obvious approach, it is not without great difficulty. First, the porous material must be compatible with the processing conditions use in applying the composite film or the asymmetric structure on the support surface. Aggressive solvents are frequently required to solution the specialty polymer employed in the separating layer. Thus, it may become necessary that the porous support be formed of a specialty material as well lest it be attacked during the composite layer deposition. Second, adhesion of the asymmetric skin to the porous support can be a major limitation. Any differences between the two composite layers with respect to thermal, mechanical, shrinkage, and swelling properties during either the membrane processing or in the membrane gas separation application can lead to cracking, delaminating, and failure akin to peeling paint. Third, the additional materials, solvents, and processing steps needed to form the composite membranes all contribute to increased product costs. Thus, a substantial performance improvement is usually necessary to make the composite membranes a viable product.

Innovations by DuPont [20, 21] enable formation of composite hollow fibers that overcome many of the problems enumerated above. DuPont co-spun hollow fibers from two different dopes, one forming a thin separating layer, the other forming the porous support structure. They applied a specialty polyimide polymer on a polyimide support made of a commercial low-cost polyimide polymer. By comparison to the unitary structure, this co-spinning forms a composite asymmetric hollow fiber composed of less than 10 % specialty polymer, with the other 90 % being a commercial polymer. Considering that as little as 1 % specialty polymer might be required in applying the separating layer to a preformed porous support, the co-spun asymmetric hollow fiber overcomes many of the other limitations noted above. First, co-spinning allows the porous support to be made of materials of the same polymer class, thereby enabling the same solvent to be employed for both polymer dopes. Second, co-spinning insures intimate polymer contacting and phase mixing at the composite interface during the polymer precipitation step. The likelihood that the specialty and commercial polymers can be from the same polymer class also increases the chances for comparable properties and thereby improves adhesion between the composite layers. Finally, co-spinning involves little additional processing facilities; save the additional dope supply system.

2.2.3 Membrane module geometry

The function of the gas separation membrane module is fourfold. First, it must contain the membrane within a pressure housing rated for the application. Second, it must have fittings to introduce feeds and to collect and distribute products leaving the device. Third, it must have internal means for gas-tight sealing between the feed and permeate sides of the membrane and with the containment vessel. Fourth, it must direct the gases in a prescribed manner uniformly over the membrane surfaces.

Module geometries generally revolve around the form of the membrane, the membrane flux, and the volumetric flows of the feed and product streams. Module geometries have also been patterned after earlier dialysis, reverse osmosis, and filtration module designs. Early flat-film designs were constructed of plates and membrane films sandwiched together in a filter press type assembly. The plate and frame design has a relatively low membrane packing density (membrane area per unit of volume). It can be used effectively in low pressure and vacuum applications, particularly for high flux membrane applications. Such applications frequently require large flow channels to accommodate the volumetric flow with minimal hydraulic resistance. These assemblies have found application in oxygen enrichment for respiratory care patients. Another flat film membrane device is shown in Fig. 2.2.

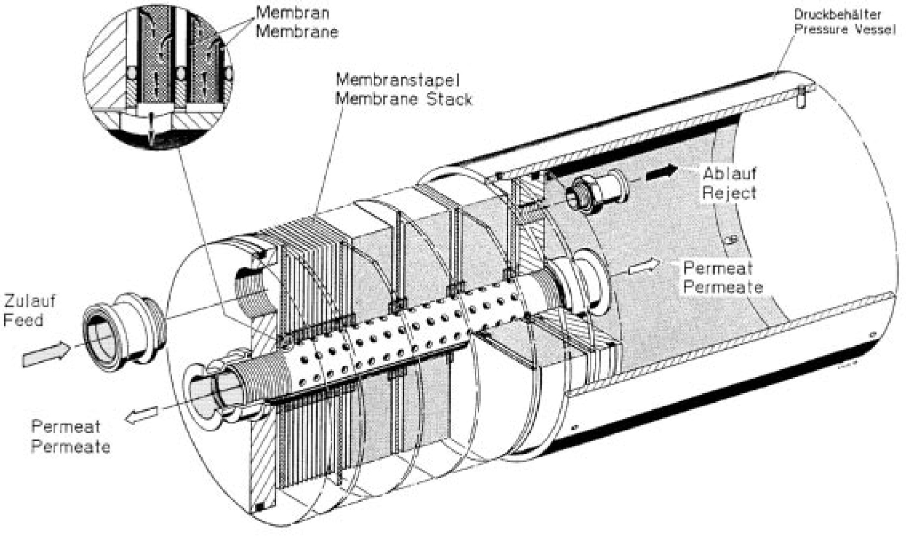

Fig. 2.2: Flat film membrane stack design by GKSS (Used with permission of GKSS.).

GKSS presently employs a flat film supported on a stack of hollow ceramic discs in their vapor recovery devices. Baffling between the discs directs the feed gas flow across the membrane-covered discs in the stack. The interior of the discs communicates with a central permeate collection conduit. The short permeate flow path of this design is particularly suited to operating the permeate side under vacuum conditions.

The more common design employing the flat sheet is the spiral-wound membrane design shown in Fig. 2.3.

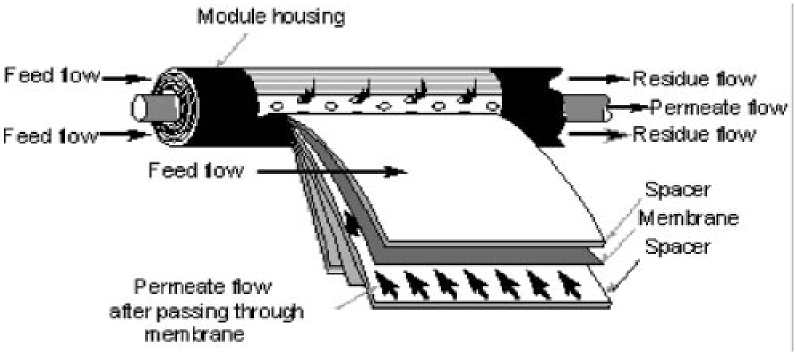

Fig. 2.3: Spiral-wound module (Used with permission of Membrane Technology & Research, Inc.).

In this design, a spacer containing permeate flow channels is enclosed in a bag or envelope made of two pieces of flat membrane sheet that are sealed on three edges. The open edge is attached and sealed to a slotted mandrel which acts as the permeate conduit and the support for the membrane assembly. Other spacers are placed between a number of leaves so attached to the mandrel. The leaf and spacer assembly is then rolled around the mandrel to form the spiral arrangement from which it derives it name. The assembly is completed by applying a covering and insertion in a pressure vessel. Feed gases pass axially through flow channels in the spacer filled gaps between the spiral leaves. Gases that permeate through the membrane pass along the spiral permeate channels to the central collection pipe. Manufacturers utilizing the spiral-wound design have some flexibility in the number and the length of the leaves they employ, spacer thickness and design, and the axial length and package diameter. Particular care is taken in the spacer design to ensure that loading arising from high flows and corresponding high pressure differentials between the axial ends do not cause deformation and damage to the spiral assembly. Some manufacturers add a perforated backing plate mounted on the downstream side of the spiral assembly to minimize distortion and damage to the spiral membrane assembly.

Hollow fibers enable substantially higher membrane area densities than are possible with either of the flat sheet designs. They also enable operation at substantially higher operating pressure and at higher trans-membrane pressure differentials. Hollow fibers also afford flexibility in module design and in alternative feed and product flow geometries. Feed and permeate flows can easily be aligned in co-current, counter-current, or cross-flow orientations as may be desired for the specific application. Module designs employing hollow fibers are often tailored to application specific requirements by adapting the fiber dimensions, the fiber lay-up orientation, and the fiber packing density. These variations enable the pressure losses in the respective flowing streams to be minimized thereby maximizing the driving forces for the separation. Figure 2.4 describes an axially oriented fiber bundle with two tubesheets separating feed and product streams.

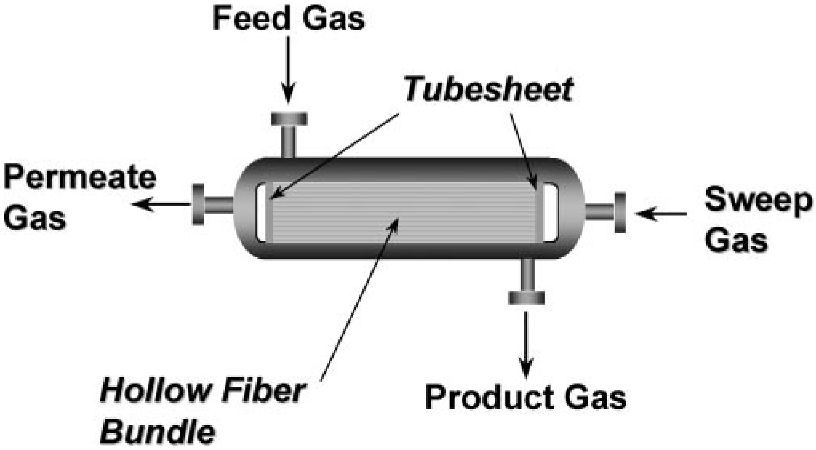

Fig. 2.4: Axially oriented hollow fiber module with bore and shell feeds (Used with permission of Air Products and Chemicals, Inc.).

This diagram shows the pressurized feed and product on the shell-side while the sweep enters and permeate leaves from the hollow fiber bores that pass through the tubesheets on either end of the device. The sweep gas shown in this diagram is not necessary for many applications and a three-ported geometry is employed. In this case, the second tubesheet is often eliminated by simply sealing or plugging the bores of the hollow fibers.

Another three-ported hollow fiber arrangement applied in a number of applications places the pressurized feed to the bore-side of the module in Fig. 2.4 and collects the permeate on the shell-side. This arrangement avoids the need for the shell to be a pressure containment device since only the end caps distributing the feed and product to and from the respective tubesheets and the hollow fibers themselves are pressurized. Hence, the shell can be made of plastic pipe or light gage metal tubing. The bore-fed arrangement can be particularly attractive when high degrees of removals of permeating species are desired in a single counter-current arrangement. The bore-fed arrangement ensures that each element of the feed necessarily must be exposed to the membrane and subjected to the partial pressure driving force before exiting at the opposite end. Thus, there can be no bypassing or channeling of flow as is sometimes possible in shell-fed axial fiber bundles [22]. However, the bore-fed module can also suffer from flow non-idealities arising from fiber-to-fiber variation in bore dimensions and in membrane transport properties. The fourth order dependence of flow on the bore diameter makes it essential that the fiber bore dimensions be precisely controlled in order to maintain uniform residence times between the multiplicity of parallel bore flow channels in the bore-fed design [23].

Uniformity and control of flow pattern on the shell-side of the hollow fiber membrane module is also important and is addressed in a variety of manners. The flexibility of the hollow fibers frequently allows movement, redistribution, and settling of fibers within the unconstrained axial bundle geometry. Varieties of means have been applied to minimize the deleterious effects on membrane module performance arising from the non-idealities in flow patterns arising from fiber movement. Monsanto introduced crimped fibers that maintained a degree of bulkiness and preserved fiber-fiber spacing within the axial bundle [24]. Toray has wound a textile fiber around the hollow fiber in a spiral fashion to provide fiber-fiber spacing [25]. Air Products recently introduced an axial bundle containing an axial textile fibers co-mingled with the axial hollow fibers to aid in preservation of flow patterns within the bundle under varying operating conditions [26].

Others have introduced helically wound or patterned fiber lay-up in the bundle geometries as a means for controlling and preserving the shell-side flow patterns within the module [27]. The use of hollow fiber fabrics have also been proposed as a means for precision spacing of the hollow fibers within the membrane module [28, 29, 30, 31]. Many of these are assembled around a central mandrel that also serves as a fluid conduit for feed introduction or product or permeate withdrawal. Modules assembled in this fashion also accommodate distributors and baffles inserted within the fiber pack to aid in the direction and control of the flow shell-side flow pattern.

As can be seen with the wide variation in module geometries already discussed, the options available for gas separation modules are limited only by the ingenuity of the designers. Current innovations stem largely from refinements on the basic designs employed in earlier in liquid phase membrane devices to deal with parameters and variables unique to gas phase separations and applications. Major distinctions between the liquid and gas phase designs arise from the phase density differences. Film boundary resistances and concentration polarization concerns that are significant in liquid phase separations are usually negligible and can be ignored in gas separators. That the gas separator designs can be radically different and independent from the traditional liquid separator geometries is reflected in a recent proposal for a carpet-like module [32]. This design proposes that very high area densities can be attained by constructing a carpet from micro-hollow fibers. Short lengths of fibers or fiber loops pass through a sealed backing material. By cutting the fibers on the underside of the backing, bores are opened on the underside of the carpet. It is expected that refinements and step-out innovations such as this will continue to drive new membrane module designs.

2.2.4 Compatible sealing materials

A number of gas-tight sealing means are typically required in the assembly, manufacture, and application of the membrane device. First, provision must be made to incorporate the membrane module into the process piping system with related manifolds and related equipment up and downstream of the membrane. This is usually accomplished via standard piping systems and is guided by piping design codes. Consideration need only be given to the wide variety of flanges, screwed thread fittings and geometries, connectors and disconnects, etc. that are available and must be either accommodated or adapted to in the design and application of membrane devices.

Seals required on the membrane elements vary with the membrane type and the module geometry. Many flat film designs employ thermal and ultrasonic welding techniques and thereby avoid the introduction or minimize the use of dissimilar sealing materials.

Most manufacturers though form at least one tubesheet around the membrane or hollow fiber in order to separate the permeate product from the feed and non-permeate product streams. Selection of the tubesheet material is typically guided by the intended application conditions, the quality of the sealing surfaces, and the manufacturing process. The tubesheet material is typically a liquid, curable resin that solidifies upon cooling or crosslinking reaction. Common materials are from the epoxy, silicone, and urethane resin families. Particular attention must be given to adhesion to and compatibility with the membrane surface. Without good bonding to the tubesheet, pressurized gases can leak through a gap between the membrane and the tubesheet. Many of the materials of choice have a solvency or plasticization effect on the membrane polymer. Thus, preserving the integrity of the microscopically thin membrane skin on the asymmetric membrane can be particularly troublesome both during assembly and in separation service. In the extreme case, the asymmetric structure may be attacked or crack during the tubesheet formation step resulting in gas leakage past the membrane. Since the tubesheet typically must form a rigid structure capable of also forming a gas-tight seal to the pressure containment vessel, any shrinkage and dimension changes during curing or set-up of the sealant or swelling during exposure to the process streams can also be a concern. In some applications, chemical degradation, temperature limits of the materials, and swelling or temperature-induced stress within membrane assembly can control the material selection or even the feasibility of the application.

Sealing between the membrane element and the pressure containment vessel is typically done with O-rings and gaskets. Primary consideration in the module design and manufacture is the provision of good sealing surfaces to accommodate the selected sealing means. Most of these seals involve compression loading of the O-ring or gasket against the sealing surfaces. Maintenance of the compressive load throughout the device's lifetime becomes the controlling parameter in the selection of these components.

Most all of the gas separations involving membranes involve the handling or formation of flammable, asphyxiants, or poisonous gases. Thus, reliable sealing of the membrane elements in the system is frequently a major environmental and safety consideration. As the size of the gas separation installations grows, there is a proportional increase in the number of elements employed and a corresponding increase in the potential for leaks. Many manufacturers have reduced the number of connections by incorporating larger and multiple membrane elements within a pressure containment vessel. Others have resorted to completely welded closures and connections to piping to eliminate then need for gaskets and seals to ambient.

Membrane manufacturers frequently have as much technology and art invested in the selection and processing of the tubesheet and sealants as in the membrane itself. Understandably, much of the details about tubesheet and gasket material selection and processing is considered proprietary and trade, or closely guarded, secret information by membrane manufacturers.

2.2.5 Module manufacture

Manufacture of gas separation membrane modules is largely a machine-assisted, labor-intensive operation. Polymer dopes are typically prepared batchwise with sufficient hold time to insure uniformity. The membrane performance is largely controlled by the polymer precipitation step and very dependent upon phase behavior and precipitation kinetics. Thus, it is essential that processing conditions be maintained as uniformly and as constant as possible if product quality and uniformity is to be preserved. For this reason, membrane film formation and hollow fiber spinning processes are usually operated continuously or for extended run times. Since the intermediate film or fiber must eventually be converted into discrete items, the continuous process is typically interrupted by collection of the membrane formed on spools or fiber skeins where it may be inventoried briefly before batch processing into the final assembly resumes.

Gas separation module assembly is typically an operator-machine interactive process, because the scale of operation cannot justify the type of automation necessary for the high volume dialysis and filter module assembly lines. This also has some advantages in enabling products to be sized and tailored to the application.

2.2.6 Pilot or field demonstration

Commercial process streams can rarely be accurately replicated in a laboratory setting. Minor and trace compounds are frequently unknown. Lubricants and corrosion inhibitors added to the process seldom appear in a feed stream composition analysis, but indeed they can make their presence known after a membrane is put into service. Other compounds may arise intermittently or occur on infrequent process upsets or under dynamic process conditions. Hence, there is no substitute for measuring the membrane performance in the intended operating setting for an extended time.

Many of the commercial membrane applications were developed by first testing performance of small membrane modules installed in pilot and field slipstreams. In recent years, commercial scale modules have been used increasingly in new application field trials. Valuable development time can be saved when representative process conditions can be tested at the larger scale. When operating conditions permit, on-line, real-time data acquired from an instrumented pilot unit can provide valuable data with which to quickly map membrane performance over a wide range of operating condition. Such units also enable quick diagnosis of the membrane's response and ability to recover from upset conditions and perturbations over the operating dynamics.

The instrumented pilot unit is not always necessary, or even justified, though. Valuable data can be measured from field samples carried to a laboratory for analysis, however particular attention must be given to the sampling and analytical process, particularly when temperatures vary greatly from the operating conditions or when reactive species are present. Accurate measurement of flow rates and compositions on all streams involved, namely feed, permeate, residue, and, if present, sweep, are essential if meaningful membrane performance data is expected. Regression of permeance and selectivity coefficients is strongly dependent on having accurate material, and especially, component balances around the membrane.

Membrane performance often changes with time. Some of this change arises from creep, plastic deformation under pressure differential loading, even in benign streams. Other changes occur as minor or trace moieties accumulate on or react with the polymer membrane over extended service time. Thus, it is recommended that membrane sample testing on the field stream should be for an extended period, at least one month, preferably for six months. Performance should be tracked over the period until the magnitude of the creep or performance change can be accurately represented since these data must be used to project the useful lifetime of the membrane elements.

It is essential that field tested samples be returned and re-tested on a well calibrated laboratory test stand to make comparison of performance changes against other experiences. Finally, after all calibration tests are completed, the membrane element should be autopsied and inspected for any observable changes in dimensions, color, effects on components, corrosion, and the like. This important step may be easily overlooked, particularly after successful permeation tests. When large modules have been tested, removal of small portions of the membrane from various locations in the geometry and re-testing on laboratory bench scale equipment can also be instructive. Frequently, subtle changes may be occurring locally that are not detected on the larger scale device due to inaccuracies, magnitude of change, etc.

The output of the pilot and field-testing program is a characterization of the membrane's performance in the intended service. Sufficient information needs to be assembled to evaluate the economics and minimize the risks associated with a first-time commercial membrane installation.

2.2.7 Process design

The process design of a membrane system involves the determination of the system size and the configuration necessary to meet the project scope and specifications. Presently this exercise is performed by the membrane supplier and application developer. Membrane suppliers have developed a proprietary membrane simulation model related to their specific membrane material, module geometry [33, 34], field and application experience, and performance parameters. Suppliers typically provide performance predictions and guarantees with their equipment and therefore often take responsibility for providing a process design package relating to their component. Thus, the process design of a membrane system typically requires close working relations and trust between the gas membrane supplier and the customer to insure that the process design package provided can be flawlessly integrated into the customer's flowsheet. Successful design and application typically requires exchange of information about operations immediately up or down stream of the membrane unit as these often interact with the control and operation of the membrane unit, particularly during start-up and shut-down.

Process controls of gas separation units typically revolve around four membrane operating parameters; temperature, pressure, flow rate, and membrane area. Since temperature adjustment frequently involves heat exchange and energy requirements for the system, it is seldom the manipulated variable. Pressure is the most commonly manipulated variable, however it is frequently limited by the available feed pressure or product pressure requirements imposed by down-stream processing. Frequently, manipulation of the permeate pressure is the only control parameter at the process designers disposal, however, its impact on product purity and recovery can impose bounds on its range. When product purities are limiting, the process designer often resorts to provision for adjusting the membrane area in service to accommodate variations in feed rates, etc. Frequently this can be done by simply blocking the permeate flow from selected membrane elements while leaving the feed pass through the remaining idled elements. This enables nearly instantaneous response to the changing performance demand.

Membrane systems are unique among gas processing technologies in that they can be easily expanded to meet changing demand. Where other technologies may require the installation of full capacity towers and vessels to be operated at fractional capacity during a product or market growth period, membranes afford the customer the option of deferring the membrane capital investment until demand is realized. Consideration only need be given for provision for tie-ins and space in the plot plan for deferred additions to the membrane unit.

2.2.8 Membrane system

Membrane units are usually supplied as a complete assembly requiring minimal field erection, save connections to process and utility piping and instrumentation systems. Fabricators and OEMs working closely with the membrane suppliers have developed

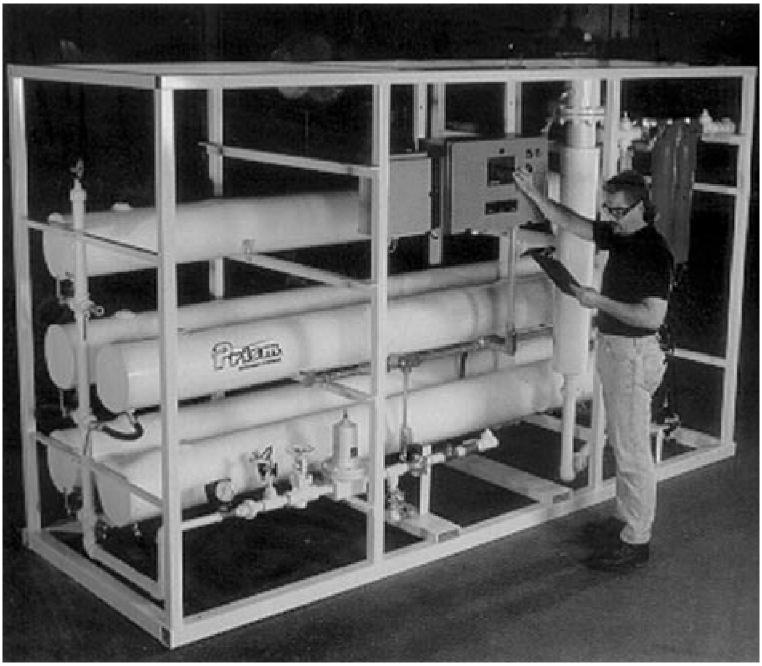

Fig. 2.5: On-site industrial nitrogen generator. (Used with permission of Air Products and Chemicals, Inc.).

membrane system packages that address a wide variety of application and industry code requirements. The nearly 20 years of experience for most membrane suppliers has afforded many membrane module and system design and cost reduction innovations to be incorporated into these packages. New applications will most certainly rely heavily on these experiences. The photographs in Figures 2.5, 2.6, and 2.7 provide examples of the diversity of these designs. Each system shown generates nitrogen, but each is operated in a very different environment and is constructed to meet the rigors unique to it.

Nitrogen generators of the type pictured in Fig. 2.5 supply gaseous nitrogen to industrial gas customers. Systems of this type can be installed in a plant warehouse or utility area to provide local nitrogen requirements. Modem connections enable the units to be monitored from remote locations.

Mobile membrane nitrogen generators of the type shown in Fig. 2.6 provide nitrogen for aircraft tire and strut inflation on flight lines. A diesel engine powers air and nitrogen compressors to deliver the 99.5 % nitrogen to a high-pressure receiver for supplying high volumes of nitrogen for aircraft servicing. Membrane elements used in such systems must be capable of handling shock and vibration associated with the movable nature of the unit and the close proximity to engine and compressors.

The system shown in Fig. 2.7 produces over 2000 Nm^3/hr of nitrogen for inerting equipment on a North Sea production platform. Such systems must be constructed for

Fig. 2.6: Mobile nitrogen generator. (Used with permission of CvB Company.)

Fig. 2.7: Nitrogen generator for an off-shore platform. (Used with permission of Air Products and Chemicals, Inc.)

operation under severe environment conditions, particularly ambient temperature extremes, ice loading, and sea water corrosion.

2.2.9 Beta site

For each successful application of new technology, there must be a first time user. The beta site or beta customer is where the new membrane application grows it wings. The beta site differs from the field test in that the installation's function shifts from one of gathering technical information and demonstrating performance to the confirmation of commercial viability and utility of the membrane in the application. The membrane supplier or application developer is dependent on identifying a customer or partner who finds the risks associated with the new technology to be minimal and acceptable for the projected rewards or benefits. The testimonials of the beta site customer largely determine the successful penetration of the technology into the new market and application. Thus, these selection and the development of a strong partnering relationship becomes a critical step in the successful introduction of a new membrane application.

Early beta site customers were frequently the parent companies or petrochemical affiliates of the membrane developers. Thus, there were convenient relationships and an internal willingness to take the risk of being a beta site. Realignment of the membrane suppliers and changes within the petrochemical industry has severed many of these relationships. Thus, two organizations must become convinced of the risk/reward merits of the new undertaking. While this provides two independent audits of the merits, the identification and negotiations for a beta site customer have become doubly more involved.

The difficulty in identifying beta sites for new applications is also shifting with the acceptance of membrane technology by the process industry. Many of the initial applications were installed with back-up provisions or in non-critical services. Industrial gas nitrogen generators were typically supported by liquid nitrogen supplies to cover the risks associated with outage or downtime. Recovery of hydrogen from a fuel gas header only bore the risk of associated capital investment with minimal operating cost penalty should there be problems with the application. The acceptance of membrane technology as a viable gas separation technique has now been largely proven thanks to over 20 years of operating experience, much of it in non-critical services [35]. With their acceptance however, membranes are being proposed increasingly for applications within the revenue stream where there is little opportunity for back-up or parallel technologies to absorb the risk of failure. Carbon dioxide removal from natural gas is an example of a membrane application that is within the main revenue stream. This application was developed to the large-scale membrane systems in operation today because of a number of small beta site installations. However, incremental and evolutionary growth is likely to be difficult, if not impossible, in some of the new membrane applications now under consideration making the identification of the beta site or beta customer ever more critical. The Starchem methanol process cited earlier is a case in point. In this case, the membrane systems are an integral part of a flowsheet intended for mega-scale operation. Its development will likely depend heavily on the costly pilot demonstration of the entire flowsheet, the risks and costs of which can only be born by a consortium of partners.

2.2.10 Cost/performance

The ultimate test of a successful membrane application is whether it is cost effective relative to other alternatives. The membrane supplier and application developer generally have good insights into the merit of the applications they pursue to develop. They would not pursue development if they did not believe there were potential rewards for their effort. Project cost principals can be applied to provide good insight into capital and operating costs and their sensitivity to cost parameters. Product value pricing demands that the supplier have good insights into the merits and potential for their products.

However, the economics of many applications are site specific; hence, the relative merits of a membrane approach can be unique to each installation. Often their true value can only be determined by the customers themselves. For example, the economics of many applications are strongly dependent upon the utility and energy pricing for the site, parameters that are likely to be known only by the customers. Frequently, industrial gas customers conduct make-versus-buy analyses in which case the equipment supplier may have little clues about the costs involved in an alternative supply chain. Thus, there is an intuitive concern among many suppliers that it is difficult to quantify value and price their products to the true customer value. For example, it is hard to capture the value for having on-site availability and independence from outages created by transportation or delivery interrupts. In some cases, particularly those involving portable or moveable gas separation units capable of remote operation, membranes offer capability where none existed before.

2.3 Commercial gas separation membrane applications

The key commercial membrane-based gas separations and suppliers are listed in Table 9 in Part I. The key features of these applications are discussed below.

2.3.1 Hydrogen separations

Hydrogen is one of the more readily membrane separated gases. It has reasonably high selectivity relative to the other gas species in the mixtures with which it is commonly associated. It is also usually present in pressurized mixtures arising from the high hydrogen partial pressures employed to promote hydrogen's reactivity. Fortunately, high partial pressures are also essential for driving membrane separations. The cost of hydrogen manufacture is closely connected to energy prices since most hydrogen is produced by reforming of natural gas and hydrocarbon compounds. Since the introduction of gas separation membrane in the late-1970's there has been the ever increasing demand for hydrogen owing largely to the higher severity in processing of heavier sour crude oils while simultaneously reducing the sulfur content of fuels to meet environmental regulations. Thus, the combination of technical feasibility plus the environmental and economic drivers has made hydrogen separations a much sought and highly successful application of membranes.

Synthesis gases formed by steam reforming typically have hydrogen:carbon monoxide ratios on the order of 3:1. Carbonylation processes however typically require a 1:1 ratio. Adjustment of the hydrogen:carbon monoxide ratio to satisfy the stoichiometric requirements of a carbonylation process [36] was the first commercial application of Monsanto's Prism® Membrane technology. The application simply involves passing the 3:1 feed mixture across the membrane while withdrawing the hydrogen rich permeate at reduced pressure. Control of the 1:1 hydrogen:carbon monoxide ratio in the carbonylation synthesis gas is accomplished under automatic process control by simply adjusting the membrane area, the feed rate, and the permeate pressure.

Hydrogenation of unsaturated hydrocarbons and hydrotreating to remove sulfur from fuels are two major consumers of hydrogen. Hydrogen supplied to reactors in these processes typically contains low concentrations of methane. Methane and other inerts formed during the hydrogenation and hydrotreating are inerts that accumulate in the reactor and reduce the hydrogen partial pressure and correspondingly, the rate of the hydrogenation reaction. Thus, it is necessary to bleed off a quantity of the reactant hydrogen to purge the reactor of these inerts. Directing these pressurized purge gases to a membrane system enables a large fraction of hydrogen lost in the purge stream to be recovered as permeate and recycled to the reactor system. Inerts are thus rejected from the process at a higher concentration. The membrane system may also enable the hydrogenation to be optimized to operated at higher hydrogen partial pressures by increasing the reactor purge rate without a severe penalty on hydrogen yield. Indeed the scheme frequently enables improved throughput or hydrogenated product quality.

Ammonia synthesis reactions are also frequently limited by the accumulation of inerts in their reactor systems. Argon, arriving with the nitrogen reactant from air, and methane, arriving with the hydrogen, accumulate as inerts within the ammonia reactor loop. The purge from the ammonia loop is typically available in excess of 100 atmospheres pressure and contains in excess of 60 % hydrogen. Membrane systems processing this high-pressure purge typically recover over 90 % of the hydrogen from these purge gas. These membrane systems typically employ two membrane units operated in series. The first recovers and recycles a large fraction of the hydrogen permeate to the final compression stage in the ammonia plant feed compressor, typically about 70 atm. In the second membrane unit, the permeate is recovered at lower pressure and is recycled to the intermediate compressor stage typically around 25 atmospheres. The rejected gas containing the concentrated inerts is typically burned as fuel in the primary reformer. The membrane systems enable ammonia plants to be optimized around higher productivity or energy savings [37, 38, 39]. The concentrated inerts can also be further processed by cryogenic or adsorption techniques for argon recovery [40, 41].

Methanol synthesis also deals with the accumulation of inerts in the reactor loop. In this case, the reformed gases supplied to the methanol reactor contain hydrogen, carbon monoxide, carbon dioxide, and small amounts of methane. The first three components react when the pressured gases are circulated over the synthesis catalyst to form methanol and water. By cooling the reactor effluent gases, methanol and water are condensed and removed, leaving the methane to concentrate in the reactor circulation loop. By removing a small purge from the loop, the concentration of methane is controlled at the expense of the reactants also vented in this stream. These purged gases are available at the reactor loop pressure, typically 60 to 100 atmospheres, thereby having sufficient partial pressures of hydrogen and carbon dioxide to drive a membrane recovery unit. The purge gas is also saturated with methanol, a slow-permeating specie for most membrane materials. Thus, it must be removed before the membrane system to avoid condensation upon concentration by removal of the fast-permeating species. This is accomplished in a water-scrubbing tower, the effluent of which can be combined with the crude methanol for product distillation. Hydrogen and carbon dioxide are then recovered from the scrubbed gases in a membrane unit and recycled to the synthesis gas compressor. Figure 2.8 is a photograph of a methanol purge gas recovery unit. Carbon monoxide unfortunately is a slow-permeating specie and therefore concentrates with the methane in the membrane reject stream that becomes fuel. Thus, as with the ammonia purge recovery, the membrane unit provides efficient recovery of valuable reactants from the purge stream and provides the methanol operator with increased productivity and flexibility in plant optimization. [42] Starchem has proposed methanol production from a synthesis gas that is rich in nitrogen and only about 90 % of the stoichiometric amount of hydrogen needed to convert the carbon monoxide and carbon dioxide. They propose the use of a membrane unit to recover and recycle hydrogen to improve the reactant stoichiometry [43].

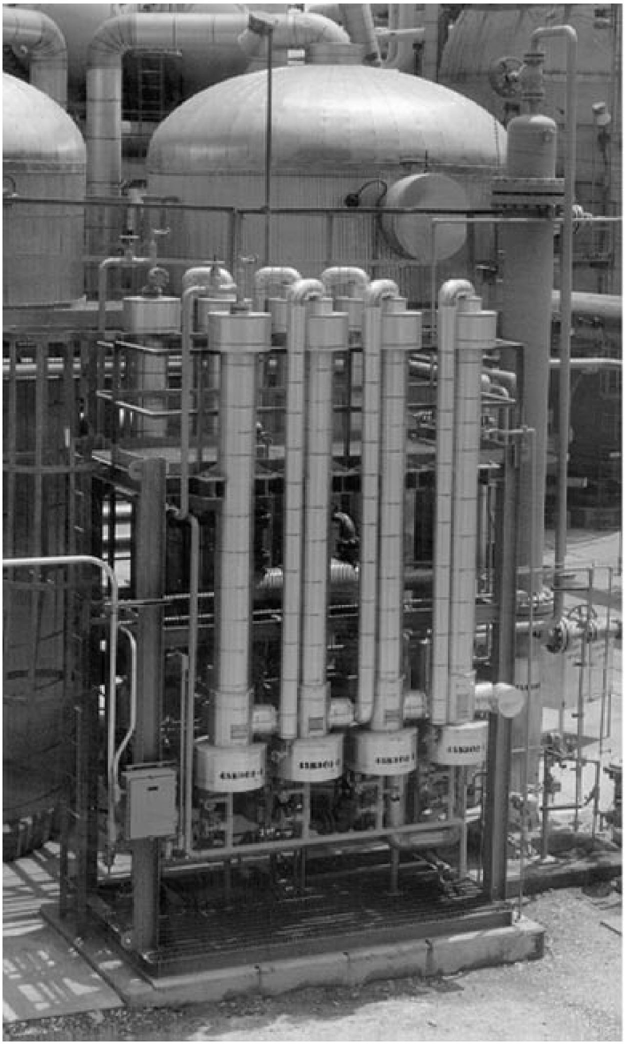

Fig. 2.8: Methanol purge gas hydrogen recovery system showing water-scrubbing tower (right) and membrane elements (center). (Used with permission of Air Products and Chemicals, Inc.)

Hydrogen recovery systems have found similar utility in oil refining. In addition to recovery of valuable hydrogen [44], the hydrogen separation system often enables the refiner to operate at higher purge rates to increase the hydrogen partial pressure in the hydroprocessing unit. This can have a significant impact on catalyst lifetime and extend run times. It also can increase the unit's throughput and product quality. Hydrogen recovered from fuel streams can also be used to supplement hydrogen production, frequently delaying or deferring the need for added hydrogen production capacity.

Membrane processing of hydrogen rich fuel gases can also improve the quality of the fuel gas since the heat content of hydrogen is about one third that of methane and hydrocarbons. Thus by removing hydrogen, the heating value of the fuel gas can be adjusted to permit use of the fuel in conventional burners and equipment sized for the heating content of natural gas or even sold as pipeline fuel.

The hydrogen separation membranes are also frequently used in conjunction with other processing and separation technologies. Production of high purity hydrogen via pressure swing adsorption (PSA) results in a waste stream containing over 40 % hydrogen. Frequently additional hydrogen and fuel values can be realized by compression of the PSA purge and processing in a hydrogen membrane system. [45, 46] Removal of the hydrogen from hydrocarbon rich fuel streams also enables recovery of condensible hydrocarbon liquids by processing the hydrogen lean fuel gases in conventional expander plants.

2.3.2 Helium separations

Like hydrogen, helium has high selectivity against most other components present in its mixtures for a wide variety of polymers. The primary source of helium is natural gas reservoirs usually in concentrations below 1 %. Considering that the low concentrations translate to low partial pressures, it can be seen that membranes find limited application in helium production since multiple stages would be required to reach even crude helium purity levels.

Membranes have found application in helium gas recovery. Deep-diving gases employ helium mixtures that become contaminated. A combination of membranes and adsorbents are employed in purification of these gases for reuse. Small membrane systems are also employed in the purification of helium used in blimps. With time, the helium gas that inflates these lighter-than-air craft becomes contaminated with atmospheric gases. These contaminants are readily rejected by operating a small compressor and membrane unit to reject the contaminants and return purified helium to the craft.

2.3.3 Nitrogen generation

Generation of nitrogen and nitrogen-rich atmospheres has become one of the largest uses for gas separation membranes. The process simply involves passing filtered compressed air across the membrane. Since oxygen permeate faster than does nitrogen, it is driven across the membrane by its partial pressure and concentrates in the permeate stream leaving reject product enriched in nitrogen. The degree of oxygen removal is simply controlled by the residence time the nitrogen product has to contact the membrane. By reducing the product draw rate from the membrane, there is a correspondingly higher degree of oxygen removal. Thus, the oxygen concentration in the nitrogen-rich gas can be simply controlled with process controller adjusting the product delivery rate to meet the specified oxygen level. Oxygen control levels vary with the application but typically fall within the 0.5 % to 2.0 % range. These can typically be achieved in a single counter-current membrane element. Concentrations below 0.1 % typically employ two or more membrane elements in series [47]. Argon, carbon dioxide, and water vapor also transport readily across the membrane. Thus, the membrane-produced nitrogen is also very dry with dew points below –80°C measured.

Most nitrogen generators process compressed air at 7 to 20 atmospheres pressure and deliver the nitrogen-rich product within one to two atmospheres of the feed pressure. The degree of pretreatment of the air supplied to the membrane varies with the membrane employed and manufacturer. The performance of some membranes is sensitive to the moisture content of the air. In these cases, the compressed air is dried before processing. Other membranes are sensitive to organic vapors and oils that are removed by carbon filters or absorption beds. Most generators are also supplied with filtration systems to remove condensate, mist, and any particulates that might plug the membrane flow channels or fiber bores. Since the permeability and selectivity of the membranes can be highly temperature dependent, most applications require the air feed to be temperature controlled in order to control the product nitrogen quality or the membrane's performance. The nitrogen product is typically delivered under pressure and flow regulation to a receiver from which it is dispensed to users on demand. The co-produced permeate is typically simply vented back to the atmosphere.

The primary utility for the nitrogen is as an inerting atmosphere, typically for fire suppression. The Critical Oxygen Concentration, the minimum level of oxygen required to sustain combustion, is typically between 9 % and 12 % oxygen for many hydrocarbons and organic compounds. Thus, maintaining an inerting supply below 3 % oxygen provides ample safety margin for many inerting applications. These levels can readily be reached with membranes having oxygen-nitrogen selectivities greater than 4. Thus membrane-generated nitrogen finds ready application anywhere flammable materials are stored, processed, or handled. Many fruits, vegetables, and produce are also preserved by maintaining them in a low oxygen atmosphere. In controlled atmosphere storage of fruits and vegetables, a low oxygen atmosphere, typically in the 2 to 10 % range, depending upon the produce, is required. This is readily accomplished by purging the storage atmospheres with nitrogen or a nitrogen-rich gas as supplied by a membrane generator.

Membrane-based nitrogen generation equipment is supplied by a number of manufacturers (see Table 9, Part I). Most are industrial gas suppliers who also use the equipment to supply smaller gas sales accounts. Membrane units are also used to supplement nitrogen supply at larger sale of gas accounts. Frequently the membrane units are sized to handle a continuous, base-load requirement with truck-supplied liquid nitrogen providing back up and covering peak demand requirements. Many of the membrane manufacturers also market membrane modules to original equipment manufacturers, OEMs. The OEMs incorporate the membrane modules and nitrogen generation capability into their own packaged equipment offerings. Since compressed air is necessary for nitrogen generation, it is not surprising that many OEMs are also compressor manufacturers and air compressor distributors. Other OEMs are specialty equipment manufacturers whose equipment is dependent on a nitrogen supply. For example, a metal processing furnace manufacturer often incorporates the inerting atmosphere generation as part of his offering. Similarly, an instrument manufacturer may incorporate a small nitrogen generation system in his package to free his product from dependence on laboratory or cylinder nitrogen supply. Their features of portability, lightweight, compact, and robustness have aided in their incorporation into nitrogen generation packages that literally can operate on land, at sea, or in the air. Following are some of the applications being served by membrane nitrogen generation equipment.

Shipboard inert gas – Nitrogen generated onboard ships is used to purge the vapor space in chemical and flammable hydrocarbon liquid vessels on chemical tankers, the seals on cryospheres on LNG tankers, and various electronic systems on navy ships.

Controlled atmosphere storage – Membranes are used to maintain controlled atmospheres in perishable warehouses, cargo containers, and the holds on banana reefer ships.

Tank and process equipment inerting – Many offshore platforms, marine terminals, refinery and chemical tank farms are supplied with membrane generated nitrogen.

Industrial Gas Sales – Many membrane suppliers are owned by or affiliated with Industrial Gas companies. They use on-site nitrogen generators to supply nitrogen to meet customer demand from baseload to total site nitrogen requirements, frequently supplemented with liquid nitrogen supply or backup.

Laboratories, photo processors, etc. – Many facilities have replaced nitrogen cylinders with small wall mounted cabinets that generate nitrogen for laboratory use from the facility's compressed air.

Metals processing – Membranes generate nitrogen for inerting many sintered-metal process furnaces, soldering station blanketing and the like.

Tire inflation – Flight line ground support carts generate and store high pressure nitrogen for aircraft tire and strut inflation. Tire molding operations and truck and automobile tire service centers are turning increasingly to generators to provide nitrogen as a replacement for compressed air for tire inflation.

Oil and gas field service – Membrane produced nitrogen is replacing air in pneumatic drilling, used in oil well servicing, and for pipeline purging.

Flare and Seal purging – Small nitrogen generators are supplying seal gas to a variety of seals on rotating machinery. It is also supplying purge to flare piping systems.

On-Board Inert Gas Generation System– OBIGGS – Nitrogen membranes fly at supersonic speeds on the USA inforce F-22. A small bleed of compressed air from the jet engine's turbine compressor is process into nitrogen to purge the fuel tanks onboard this aircraft. OBIGGS is gaining increasing interest for military and commercial aircraft with the discovery of a fuel tank explosion as the probable cause of the TWA Flight 800 disaster.

2.3.4 Acid gas separations

Figure 2.1 shows that the acid gases carbon monoxide and hydrogen sulfide have permeabilities in polyetherimide film that are about 20 times those of methane, nitrogen, and carbon monoxide, others gases they frequently accompany in mixtures. Indeed, many commercial gas separation membranes have sufficiently favorable selectivities and permeance to make their application viable in a variety of applications. Commercial acid gas removal applications include pipeline grade natural gas production [48, 49], carbon dioxide recovery and recycle in enhanced oil recovery (EOR) [50, 51, 52], methane recovery from landfill and biogas, [53, 54], and carbon dioxide recovery from flue gases [55, 56].

Figure 2.9 depicts the performance of a typical acid gas removal membrane. The graph provides operating lines for several feed composition levels and predicts combi-

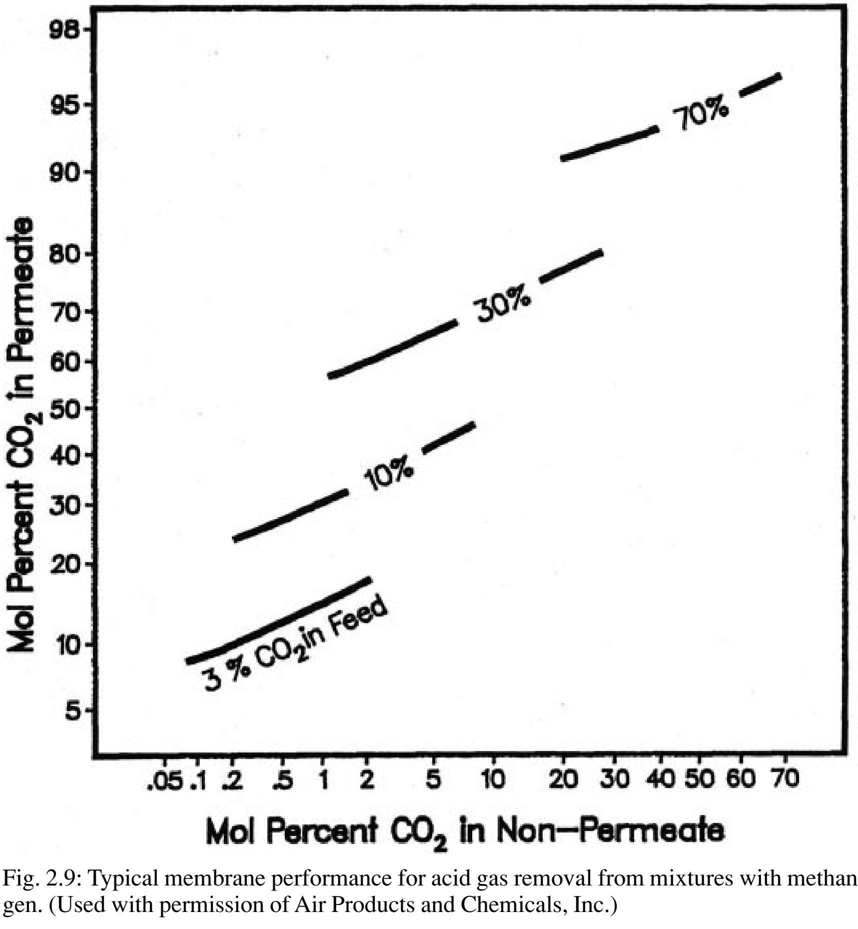

Fig. 2.9: Typical membrane performance for acid gas removal from mixtures with methane or nitrogen. (Used with permission of Air Products and Chemicals, Inc.)

nations of the permeate and non-permeate product composition that can be expected when the membrane feed to permeate pressure ratio is greater than 20.

Inspection of this diagram reveals the dilemma associated with membrane applications for acid gas separations, namely that it is difficult to produce high purity products in either permeate or non-permeate at high recoveries with a single membrane stage. Thus, it is necessary to have an alternative application for the impure co-product, or resort to a more complicated process involving compression of the permeate to feed successive membrane stages to achieve high degrees of separation [57].

Study of the diagram reveals that processing a typical raw natural gas to a pipeline grade natural gas containing less than 2 % carbon dioxide, while rejecting carbon dioxide at greater than 90 % purity would require at least three membrane stages with permeate compression between each stage. The economy for such makes it practical in only a limited number of applications.

Despite this limitation, membranes are finding increasing application in acid gas removal. The successful applications depend upon identifying utility for the low-purity co-products in another service or application. For example, processing a 20 % CO_2 feed to pipeline grade natural gas produces a medium-heating quality fuel that is used for power generation. In another case, a membrane unit produces a high CO_2 permeate gas suitable for injection into an oil reservoir for enhance oil recovery while the co-product is processed further with a conventional amine sweetening process.

2.3.5 Gas dehydration

The capability of membranes to dry gases was recognized in the early hydrogen, acid gas, and nitrogen membrane applications. Indeed some nitrogen generation systems were marketed for their ability to produce a very dry product suited for purging of cryogenic and LNG equipment. It was recognized early that a membrane's productivity of dry gas was dependent upon the creation of sufficient permeate volume to maintain the very low partial pressure driving force associated with a product containing only parts per million of water. Monsanto introduced the Cactus® membrane air dryer in 1987 that relied on a different, higher flux membrane on the dry product end of the separator [58]. This allowed for the internal generation of counter-current sweep flow of dried product to create a good partial pressure driving force along the dryer length. Other dryers have since been introduced by a number of suppliers that rely on a four-ported membrane design as shown in Figure 2.4 to provide a controlled amount of sweep gas.

Most membrane dryers such as the Cactus® Membrane Air Dryer line shown in Fig. 2.10 are marketed to OEMs and compressor and instrument distributors. These devices process filtered compressed air to deliver compressed air having dew points as low as –40°C at 10 atmospheres pressure.

Using membranes for drying natural gas was suggested as early as 1984 [59], but it was 1996 before the concept became reality when Air Product's Permea organization

Fig. 2.10: Cactus® membrane compressed air dryers. (Used with permission of Air Products and Chemicals, Inc.)

introduced a swept dryer design that was capable of drying gases to pipeline specifications at pressures as high as 70 bara [60]. Since then several demonstration units with capacities as high as 200 KNm^3/day have been installed.

The high pressure dryer has also found application in high-pressure compressed air systems onboard US Navy vessels [61]. These dryers are typically operated between compressor stages at 30 to 70 bara pressures and the dry product returned to the next compression stage for final boost to the 200 to 330 bara receiver pressure.

2.4 Developing membrane applications

2.4.1 Oxygen and oxygen enriched air

All nitrogen generators necessarily produce an oxygen enriched air, OEA, co-product, however it is generally vented to the atmosphere. This is probably because the OEA is at low pressure, varies in composition due to process controls on the nitrogen generator, and volumes are small in comparison to meaningful OEA application requirements.

One commercial application generates OEA for use in intermittent catalyst regeneration. This application is unique though as there is also an on-site application for nitrogen generation. The installation serves as a beta site for the OEA application.

Membranes have also been employed to produce OEA for ozone generators. Most attempts have involved the OEA co-product from compressed air driven nitrogen generators. Since ozone generation is proportional to oxygen concentration and is favored by atmospheric pressures operation, feeding the OEA to an ozone generator would appear to be a logical application. However, the economics are highly dependent on recovering value from the nitrogen co-product stream. The application involves feeding the membrane with dry compressed air since any moisture present in the feed co-permeates with the OEA and interferes with the ozone generation.

Only a small amount of the oxygen supplied is converted in an ozone generator. In a typical application, the ozone rich stream is processed in an absorber or contactor tower to decompose organics in waste streams. Vent gases leaving such equipment are rich in oxygen when the ozone generator has been fed by OEA or oxygen. Thus, there has been interest in recovery and recycle of these vent gases to the ozone generator. Air separation membranes have been operated in such a recycle arrangement to enrich the OEA to as high as 60 to 70 % oxygen. At these levels, the ozone generator becomes very effective and more than doubles in productivity over an air feed. Such is the good news. Unfortunately, any residual ozone in the vent gas recycle stream also attacks the polymeric membranes. With time, even ppm levels of ozone have a cumulative, irreversible, degrading effect on the membranes and shortening of their useful life. Design of guard beds, ozone destruct catalysts, and the like to protect the membranes have been successful during normal operation, however control systems designed for low ozone levels were not sufficiently responsive in detecting and responding to overload and upset conditions before damaging the membranes in the demonstration unit.

OEA production from air is favored by vacuum driven membranes operating at low oxygen recovery. In this case, the OEA purity is simply a function of the membrane's selectivity and the vacuum level at which the OEA permeate is withdrawn. Unfortunately, the high selectivity membranes employed in nitrogen generators have low flux and would require huge membrane areas at the sub-atmospheric pressure. Presently high flux materials are being used but OEA purities are limited to less than 30 % oxygen. There is much research activity in pursuit of higher flux, higher selective membranes that will bear watching for this application.

2.4.2 Nitrogen rejection from natural gas

A number of membrane developers and suppliers are pursuing nitrogen rejection from natural gas with high flux, low selectivity membranes. Modest nitrogen reduction (30–50 % nitrogen removal) in the pressurized natural gas has been demonstrated at a beta site with plasma treated polydimethlysiloxane membranes supplied by Neomecs. [62] Permeate from the nitrogen reduction membrane unit is nitrogen enriched. As the acid gas removal cases discussed above, this application also depends upon the disposition of this low energy gas.

2.4.3 Nitrogen enriched air (NEA)

Compact Membrane Systems is actively pursuing NEA as a replacement for Exhaust Gas Recycle, EGR, as a NO_x abatement measure on diesel engines. The CMS membrane is high flux, low selectivity capable of enriching the turbocharged engine air to 82 to 84 % nitrogen. Such levels have been demonstrated as being effective in substantially reducing NO_x components [63].

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3 State-of-Art of Pervaporation Processes in the Chemical Industry

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3.1 Introduction

In 1917 P.A. Kober [1] published a paper in which he described his observation that "a liquid in a collodion bag, which was suspended in the air, evaporated, although the bag was tightly closed". Kober was not the first researcher to observe this phenomenon that a liquid can evaporate through a tightly closed "membrane", but the first to realise its potential for the separation of liquid mixtures which otherwise are difficult to separate, and to separate them under moderate conditions by means of a membrane. He introduced the terms "Pervaporation", and "Perstillation", and the first term is today in use to describe in general a process in which one component out of a fluid mixture is selectively permeating through a dense membrane, driven by a gradient in partial vapour pressure, leaving the membrane as a vapour, and being recovered in a condensed form as a liquid.

In the years following Kober's publication a few papers were published describing membranes and processes for pervaporation. The related phenomena were mainly investigated in research laboratory but without looking intensely for any practical applications. This was mainly due to the lack in understanding of membrane processes in general and the absence of suitable membranes. Later during the fifties the picture changed and a considerable effort was devoted in industrial research for effective membranes in order to introduce pervaporation as an additional industrial separation process. The interest focussed on membranes and processes for the separation of different classes of hydrocarbons and of isomers [2, 3, 4] and a number of patents were granted [5, 6]. Membrane materials disclosed were natural and synthetic rubbers, cellulose esters and ethers, and several treated and untreated polyolefines. None of these early membranes, however, could be applied in any industrial process, due to insufficient flux and selectivity.

With the development of the integral asymmetric cellulose acetate membranes for desalination of saline water a few researchers turned again to pervaporation [7, 8, 9]. But it was not before 1982 that a first pervaporation membrane useful for the removal of water from organic liquids on an industrial scale was developed and introduced into the market by a small German company, GFT (Gesellschaft für Trennverfahren [10, 11, 12]. In 1983 a first plant started its operation for the dehydration of azeotropous ethanol in Brazil, with a capacity of 1200 l/d of anhydrous ethanol. This plant was followed by others [13, 14], first for the production of anhydrous ethanol only.

Following the experience gained in ethanol dehydration, in 1988 the first plant started its operation in the chemical industry for the dehydration of an ester. Soon other application for dewatering followed, covering today a broad range of solvents and solvent mixtures, especially those forming azeotropes with water. In 1994 a first plant started its operation in which water is continuously removed from a reaction mixture, in order to shift the reaction equilibrium towards the wanted product, in this case a diester, and, by nearly totally converting one of the educts, to facilitate the downstream purification of the product.

Removal of water from organic mixtures by pervaporation or vapour permeation is now a widely accepted state-of-art technology. Meanwhile new membranes have been developed which allow to separate simple alcohols like methanol or ethanol from their mixtures with organic solvents whereby these mixture are virtually anhydrous. The first industrial plant of this kind started its operation in 1997 [15], separating methanol out of its azeotropic mixture with TMB (trimethylborate). Many commonly used organic solvents form azeotropes with methanol which cannot always easily be separated. The respective simple esters of methanol and ethanol also form azeotropes with the alcohol, and the often used water wash for splitting of the azeotrope may lead to unwanted hydrolysis. It thus can be assumed that the importance of this type of separation will probably increase in the future.

Removal of low volatile organic components (VOC's) from aqueous streams by means of pervaporation through organophilic membranes has been tested [16, 17, 18, 19] but not yet found an industrial application. If the aqueous stream is waste water competing processes like air or steam stripping, or distillation, and biological treatment are well introduced and usually cheaper, especially as the substances recovered from a mixed waste water stream are low in volume and not of a high value as they have to be further treated and purified. When the substance to be separated from the aqueous mixture has a high value and is otherwise difficult to be recovered this application of pervaporation [20, 21] may gain new interest in the future. The separation and recovery of aroma components from natural products or from microbiological production is one such example which is widely investigated in research laboratories, although still no industrial application does exist.

Separation of low volatile organic components (VOC's) from gas streams through organophilic membranes, however, has become an accepted and widely used technology. Monomers like ethene, propene, or vinylchloride are recovered from strip gas or waste gas streams and recycled to the upstream process, and gasoline vapours are separated from waste air streams in tank farms. In these applications the recovered material is sufficiently pure for further use and has a high value as it is otherwise lost and wasted e.g. by incineration. These application of vapour permeation will be dealt with in a separate chapter.

Separation of different organic components from each other is still a matter of laboratory investigation. In the past 15 years considerable efforts had been devoted to develop polymeric membranes to separate, for example aromatic hydrocarbons from aliphatic ones which resulted so far in numerous patents (e. g. by Exxon [22, 23]), or olefines from paraffines or to separate isomeres, e.g. para and ortho xylenes, from each other So far none of these developments has lead to industrial applications, as selectivity and stability of the polymeric membranes are still insufficient. With the further development of new membranes which incorporate adsorbents or absorbents like specific activated carbon or zeolites this may be changed in the next future.

3.2 Principles and calculations

3.2.1 Definitions

Pervaporation, Vapour Permeation and Gas Permeation are very closely related processes. In all three cases the driving force for the transport of matter through the membrane is a gradient in the chemical potential which can best be described by a gradient in partial vapour pressure of the components. The separation is governed by the physical-chemical affinity between the membrane material and the species to pass through and thus by sorption and solubility phenomena. The transport through the membrane is effected by diffusion and the differences in the diffusivities of the different components in the membrane are important for the separation efficiency, too. The differences between the three processes are found in the phase and the thermodynamic conditions of the feed mixture:

Pervaporation:
A liquid feed mixture is in contact with one side of the membrane, all partial vapour pressure are at saturation. The gradient in partial vapour pressure between the feed and the permeate side of the membrane is maintained by a reduction of the permeate side partial vapour pressure. The permeate leaves the membrane as a vapour and is usually condensed, and removed as a liquid. The heat necessary for the evaporation of the permeate has to be transported through the membrane, and this transport of energy is coupled to the transport of matter. The evaporation enthalpy is taken from the sensible heat of the liquid feed mixture, which leads to a reduction in feed side temperature.

Vapour Permeation:
The feed mixture is in the vapour phase, the partial vapour pressure at least of the critical (better permeating) component in the feed mixture is at or close to saturation. The gradient in partial vapour pressure is maintained by a reduction of the permeate side partial vapour pressure, too. The permeate leaves the membrane as a vapour and at least the critical (better permeating) component in the permeate can be condensed and removed as a liquid. Due to changes of saturation conditions (temperature or pressure) with changing composition of the feed mixture some of the feed vapour will condense on the membrane surface and will be separated by pervaporation.

Gas Permeation:
The feed mixture is in the gas phase (the temperature for all components is above the critical temperature), the partial vapour pressures of all components in the feed mixture are far below saturation. The gradient in partial vapour pressure is usually maintained by an increase of total feed side pressure. The permeate cannot be condensed and is removed as a gas.

Therefore all three processes are but different aspects of the same transport mechanism and the same membranes are used at least for pervaporation and vapour permeation, sometimes even for gas separation. Today wherever the term “pervaporation” is used it should be well understood that it includes at least “vapour permeation” as well.

Transport through the membrane can best be described by a so-called “Solution – Diffusion – Mechanism”. In this mechanism it is assumed that a component of the feed having a high affinity to the membrane is easily and preferentially adsorbed and dissolved in the membrane substance (Fig. 3.1). The better soluble a component is, the more matter is dissolved in the membrane and the more the membrane will swell and change its composition. Swelling effects are the highest in pervaporation, as a high density fluid is contacting the feed side of the membrane, they are somewhat lower in vapour permeation and of lesser importance in gas separation due to the much lower density of the feed mixture.

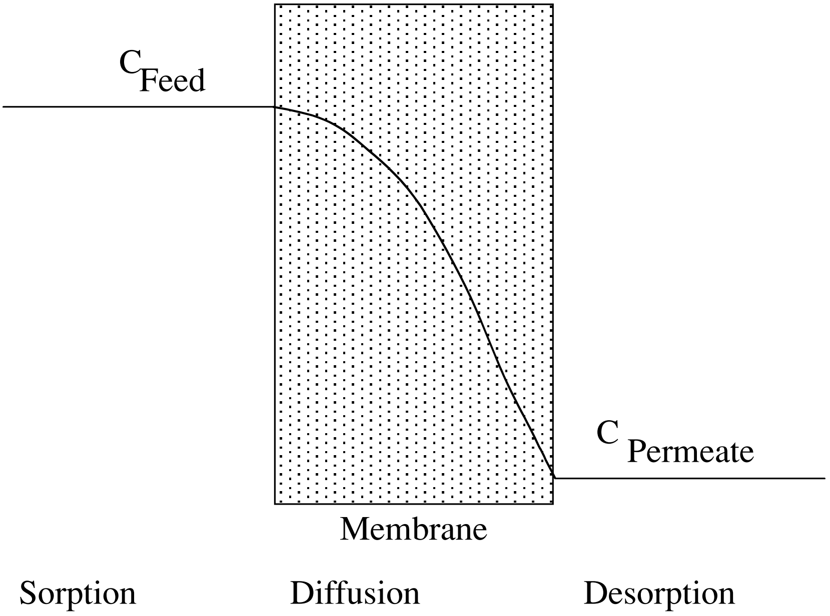

Fig. 3.1: Solution diffusion mechanism.

Following a concentration gradient the components migrates through the membrane by a diffusion process and are desorbed at the downstream side of the membrane into a vapour phase. In vapour permeation and gas separation the phases on both sides of the membrane are identically gaseous (or vaporous). In pervaporation the components passing through the membrane are sorbed out of a liquid phase but desorbed into a vapour phase, as the permeate side partial vapour pressures are maintained below the respective saturation values existing on the feed side. The energy for the phase transition, the evaporation enthalpy has to be transported through the membrane as well, which makes pervaporation unique compared to all other transport processes involving membranes.

Substances with lower or no solubility in the membrane material cannot be dissolved or reach only low concentrations and thus low transport rates. As the diffusion coefficients of small molecules in a polymeric matrix do not differ too much, the separation characteristics of the membrane is primarily governed by the different solubilities of the components in the membrane material and to a lesser extend by their diffusion rates. When a smaller molecule is better dissolved in the membrane substance solubility and diffusion enhance each other. This is at least the case in dehydration processes where water is both the better soluble and faster diffusing component. In the removal of VOC's from gases where large molecules are removed and the larger molecule is the better soluble one, the diffusion step may counteract solubility and reduce the overall selectivity towards smaller molecules.

3.2.2 Calculation

Any mathematical modelling of pervaporation has to start with simplifications. At first it is generally assumed that the respective sorption-desorption equilibria are established for all components at both sides of the membrane and that they follow Henry's law.

$$c_i^f = P_i^0\, k \tag{1}$$

and

$$c_i^p = P_i^p\, k \tag{2}$$

where c_i^f and c_i^p, denote the respective concentration of the component in the membrane at the feed and the permeate side, P_i^0 the saturation partial vapour pressure in the feed and P_i^p the respective partial vapour pressure at the permeate side, and k a constant, depending on the temperature and nature of the system.

As sorption equilibria exist on both sides of the membrane, the overall rate of the transmembrane transport is determined by the diffusion step only. Fick's law can be used to describe the diffusional transport of a component i through the membrane

$$J_i = D_i\, dc_i/dx \tag{3}$$

where Ji is the partial flux or permeation rate of the component, D_i its diffusivity or diffusion coefficient and dc_i/dx is the concentration gradient across the membrane.

The diffusivity of a component dissolved in a liquid or in a polymeric film depends strongly on its concentration. As the concentration of the dissolved species change from the feed to the permeate side of the membrane, concentration depend diffusion coefficient have to be introduced into eq. (3). Different expressions have been proposed to relate diffusivity to concentration. One of the more commonly used relations is

$$D_i = D_{i0} \exp(\tau\, c_i) \tag{4}$$

with D_{i0} the diffusion coefficient at zero concentration, c_i the respective concentration in the membrane and τ the plasticing coefficient. Substitution of eq. (3) into (2) and integration between the boundary condition c_i^f, and c_i^p (concentration at the feed and permeate side of the membrane) and 0 and L (thickness of the membrane) results at steady state in

$$J_i = D_{i0} / (\tau\, L) (\exp (\tau\, c_i^f) - \exp (\tau\, c_i^p)) \tag{5}$$

Substituting eq. (1) into eq. (5) leads to

$$J_i = D_{i0} / (t\, L) (\exp (t\, k\, P_i^0) - \exp (t\, k\, P_i^p)) \tag{6}$$

and the permeability Q_i of the membrane is given by

$$Q_i = J_i\, L / DP \tag{7}$$

or

$$Q_i = D_{i0} / (\tau\, \Delta P) (\exp (\tau\, k\, P_i^0) - \exp (\tau\, k\, P_i^p)) \tag{8}$$

where ΔP is

$$\Delta P = P_i^0 - P_i^p \tag{9}$$

the difference in partial vapour pressure across the membrane.

If a low vacuum is maintained at the permeate side, the partial vapour pressure of the component in the permeate can be kept sufficiently close to zero and be neglected compared to that of the feed side pressure. Hence, eq. (6) and (8) simplify to

$$J_i = D_{i0} / (\tau\, L) (\exp (\tau\, k\, P_i^0) - 1 \tag{10}$$

and

$$Q_i = D_{i0} / (\tau\, \Delta P) (\exp (\tau\, k\, P_i^0) - 1 \tag{11}$$

Permeability Q_i for a single component can be measured by a pervaporation test, D_{i0}, and k can be determined in sorption experiments, whereas τ cannot be measured directly and is used as an adjustable parameter. Thus, with the knowledge of the permeabilities of the single components in the membrane and the respective temperature dependencies of the constants, selectivity and total flux for a given membrane and a given feed mixture could be calculated.

Unfortunately, such an approach is practically for the separation of inert gases in polymeric films only, where no interaction occurs between the membrane and the migrating molecules. As soon as one of the components of the feed mixture interacts with the membrane material and is dissolved in the membrane to any larger extent effective flux and selectivity cannot be calculated from single component data [24]. This is due to the change of the membrane material by the dissolution of at least one of the components in the polymer. When a first small portion of a substance is dissolved in the membrane material the latter starts to swell and change its properties. Thus the next portion of the same substance is dissolved into a different membrane than the first one. When different substances get into contact with the membrane material out of a feed mixture strong coupling effects can be observed for both solubility and diffusion [25].

One substance A may have a high affinity with and be highly soluble in the membrane polymer. This will lead to high swelling and eventually to a high permeability, whereas another substance B may not be soluble at all and thus its permeability may be close to zero. By measuring the single component data and calculating the selectivity as the ratio of the permeabilities a high, so-called “ideal” selectivity will result. When bringing the binary mixture of A and B in contact with the membrane, however, no selectivity at all may be measured, as component B will now be easily passing through the membrane highly swollen by component A. This coupling of solubility, swelling and flux between the two components is usually dependent on the concentration of A and B in the mixture, and may even occur at fairly low concentrations of substances with a high swelling potential. It could be shown for polyvinyl alcohol membranes [26] that simple alcohols like methanol, ethanol, or 2-propanol are nearly insoluble in this membrane material, whereas water is easily dissolved and swells the membrane. With increasing water content in the feed mixture, more and more of the alcohol is dissolved in the water swollen membrane. The solubility of the alcohol goes through a maximum and drops with decreasing alcohol content in the feed.

Similar behaviour is observed for the diffusion coefficient. Calculation of flux and selectivity for a membrane even for a simple binary mixture from single component data therefore requires measurements of solubility and diffusion for both components over the whole range of composition and of temperature of the mixture with high accuracy. For any practical application and engineering design of a pervaporation plant such an approach is not realistic.

For a membrane with in direct contact with the liquid feed the Henry’s law is probably not valid and the equilibrium concentration in the membrane at cannot be calculated. Furthermore by the transport through the membrane the fluid layer directly adjacent to the membrane surface will be depleted of the better permeable component, and its concentration will be lower than that in the bulk of the feed mixture. The same effect does exist for the temperature (Fig. 3.2), thus both temperature and composition in the boundary layer are different from that in the bulk of the feed and not known. There may be an additional resistance for the transport of matter and energy from the fluid phase into the membrane. A similar transport resistance may exist at the permeate side for the desorption step. For real membranes the pressure directly at the permeate side of the membrane cannot be measured, as these membranes have a porous support and the pressure loss in the pores depends on pressure and volume flow of the permeate and thus on the operation parameters of the process. All these additional transports resistances and their dependence on composition and temperature have to be known for an exact model calculation. Therefor any equation and calculation derived from a physical-chemical model would need a large number of adjustable coefficients which have to be determined experimentally for the respective feed mixture and operation conditions. Such model would be very complicated, and still of insufficient accuracy.

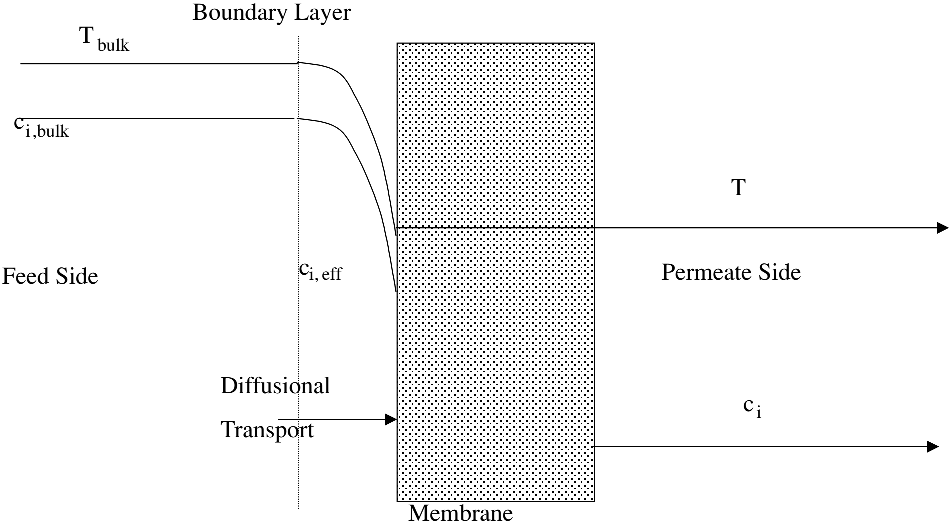

Fig. 3.2: Real conditions, feed side mass and heat transport resistance.

The design of any real pervaporation and vapour permeation installation has thus to be based on experimental data measured in the laboratory under conditions as similar as possible to those of the later full size plant. These conditions include the flow regime of the feed mixture, the temperature and the geometry of the feed side, the composition and nature of the feed mixture, the permeate side geometry and partial vapour pressure. From the experimental data the partial transmembrane fluxes of all components and thus the selectivity can be determined as a function of composition, temperature and permeate side conditions for the respective mixture and geometry. In practice the permeate side conditions (total pressure, condensation temperature) are kept as close as possible to those expected in the final plant, thus changes of this parameter do not need to be considered.

Any suitable equation, which still can have resemblance to a transport equation but does not need to refer to any physical model, can then be used to describe the experimental results with sufficient accuracy, preferentially with a minimum of adjustable coefficients. Simple binomial functions are commonly in use and it is tried to reduce even multi-component mixtures to binary systems by calculating the partial flux of the better permeable component on one side and summarising the lesser permeable components as one retained component. Equations of the form

$$J_{\text{transported}} = AX + BX^C \qquad (12)$$

and

$$J_{\text{retained}} = D(1\text{-}X) + E(1\text{-}X)X \qquad (13)$$

have proven to be quite useful to describe the dependence of the partial flux of the transported and retained component for dehydration applications, respectively. X is the mass (or molar) fraction of the better permeable component, $J_{\text{transported}}$ is the partial flux of the better permeable component (e. g. water in hydrophilic pervaporation), J_{retained} the flux of the non or lesser permeating component (one or several organic substances in dehydration), and A, B, C, D, E are adjustable coefficients which have to be determined from tests which each individual mixture.

The dependence of the fluxes on temperature can be described with a simple Arrhenius-type equation.

$$J_T = J_0 \ \exp\left(E_A/R\ (1/T - 1/T_0)\right) \qquad (14)$$

or

$$J_T = J_0 \ \exp\left(T_A\ (1/T - 1/T_0)\right) \qquad (15)$$

with J_T and J_0 the fluxes at temperature T and the reference temperature T_0, R the gas constant and E_A and T_A the apparent activation enthalpy or activation temperature. In some cases, however, the apparent activation enthalpy (E_A) or apparent activation (T_A) is not a constant, but may depend on the mass or molar fraction X as well and will have to be described by a two parameter linear or exponential function.

From the total flux

$$J_{\text{total}} = (J_{\text{trans}} + J_{\text{ret}}) \qquad (16)$$

and the concentration of the better permeable component in the permeate

$$Cp = J_{trans} / (J_{trans} + J_{ret}) \qquad (17)$$

$$Cp = J_{trans} / J_{total} \qquad (18)$$

the partial fluxes of the transported and retained component can easily be calculated.

For the above equations (14) and (15), 5 constants have to be determined experimentally in order to describe the flux and selectivity of a membrane for one feed mixture at a given temperature. This means that flux and permeate composition for at least 5 different concentrations at constant temperatures have to be measured. For the determination of the activation enthalpie or activation temperature flux and composition of the permeate has to be measured at two different temperatures, but constant concentration, if the activation temperature depends on the feed concentration, two more measurements are necessary.

Within the validity of the test parameters, however, the performance of the membrane can then be calculated with sufficient accuracy even for large industrial plants.

Such calculations are generally performed stepwise by separating the total membrane area into sufficiently small membrane increments, assuming constant composition and temperature for each small membrane increment. The amount of the permeate passing through the membrane and its composition are calculated as well as the loss in temperature caused by the evaporation of the permeate. The temperature and composition of the residual feed stream leaving the first increment now gives the respective values for the second increment. By means of the above Arrhenius equation the reduction of flux caused by the temperature drop for each step or membrane increment is calculated, too. The total membrane area required for a wanted separation is then obtained as the sum of all membrane increments.

A certain ratio of partial vapour pressures of the better permeable component at the permeate and at the feed side is usually fixed and maintained in the laboratory experiment. This ratio has to be kept as a minimum for the last increment of the membrane area in the calculated installation and the resulting condensation temperature, otherwise a transfer of the laboratory data to the full scale plant will lead to large errors. By an additional efficiency factor corrections for any differences between the more ideal conditions in the laboratory experiment and the more realistic conditions in an industrial plant may be introduced.

In vapour permeation similar empirical relations as above may be used, sometimes it is sufficient to simplify the equations into a form

$$J_{transported} = R_t \; \nabla P_{transported} \qquad (19)$$

$$J_{retained} = R_r \; \nabla P_{retained} \qquad (20)$$

with ∇P the gradient in partial vapour pressure and R the experimentally determined permeability. For some system this permeability may have a constant value, for others it has found to be a function of temperature and of the concentration of the better permeable component in the feed.

Calculation of any practical installation is performed in analogy to the method as described above for pervaporation plants.

For small concentration changes between feed and retentate and for a first estimation of the membrane area necessary for a specified separation a simple but useful relation can be derived.

$$A = M/t \ \ 1/J_0 \ \ \ln (C_{feed} / C_{product}) \tag{21}$$

Here

A denotes the membrane area,
M the amount of feed to be treated during time t,
J_0 is the measured flux at a certain concentration divided by that concentration,
C_{feed} the concentration of the critical component in the feed
$C_{product}$ the concentration of the critical component in the product

Equation (21) assumes constant temperature of the process, infinite selectivity of the membrane (only the removed component is passing into the permeate), no loss of matter from feed to product (constant volume of the feed, or small change from feed to product concentration) and a linear relation between the concentration of the better permeable component in the feed and its flux through the membrane. As long as these limitations are kept in mind this relation is quite useful for a first estimation of membrane area for a given separation problem, especially in vapour permeation. For a given installation with fixed area of a membrane the influence of changes in one of the parameters like plant capacity (feed treated per unit of time), feed or product concentration on the on the other parameters of the plant can be estimated. Eq. (21) allows in addition a direct scale up from a laboratory or pilot plant test to a full size plant, if the same membrane is used and all parameters are the same in the small and large plant.

3.2.3 Permeate side conditions

In pervaporation and vapour permeation processes the partial vapour pressures of the components at the feed side are fixed by nature of the components, composition, and temperature of the feed, whereas the total pressure is of no influence, as long as the liquid mixture can be regarded as incompressible. Only by increasing the temperature of the liquid mixture the partial vapour pressure can be increased for a given feed mixture. Therefore the driving force for the transport of matter through the membrane is applied and maintained by reducing the partial vapour pressure at the permeate side.

The influence of the permeate side partial pressure can be derived from a generalised form of Ohm's law

$$J_i = c_i \; u_i \; \text{grad}\, \mu_i \qquad (22)$$

with J_i the Flux of species i, u_i its mobility, c_i its concentration, and grad μ_i the gradient in the chemical potential. With the thickness L of the membrane and the mobility

$$u_i = D_i \,/\, R \; T \qquad (23)$$

one gets

$$J_i = c_i \; D_i \; \Delta \mu_i \,/\, (R \; T \; L) \qquad (24)$$

Considering only the partial vapour pressure as the driving force one obtains

$$J_i = c_i \; D_i \,/\, L \; \ln \,(\, x_i \; \gamma_i \; P_{if} \,/\, y_i \; P_p) \qquad (25)$$

x_i and are the molar concentrations of species i at the feed and permeate side, γ_i is the respective activity coefficient in the feed mixture, P_{if} is the vapour pressure of the pure component i and P_p is the total pressure at the permeate side. In a practical application x_i is fairly small (the component has to be removed from the feed), but y_i may be close to unity for high selective membrane. The value in brackets shoul be somewhere between seven and ten.

Different means have been proposed in order to reduce the permeate side partial vapour pressure (Fig. 3.3):

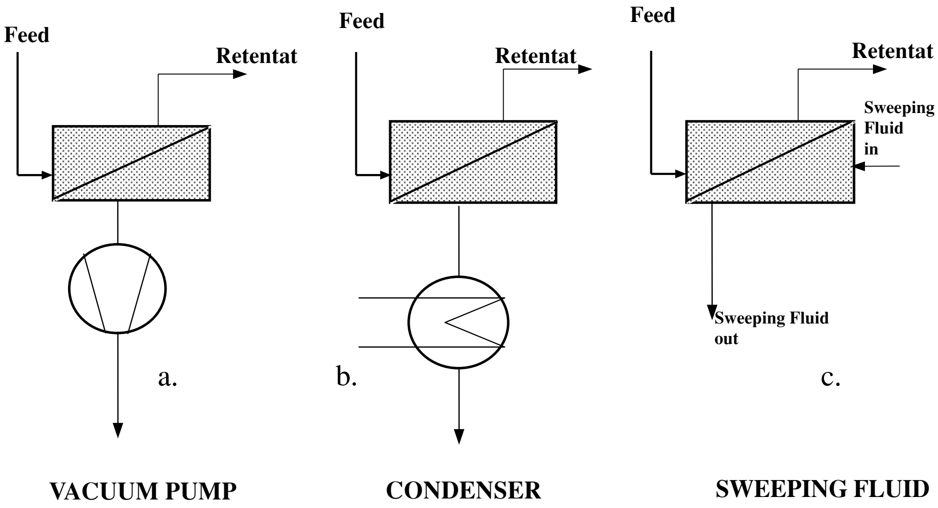

Fig. 3.3: Reduction of permeate side partial vapour pressure.

a. All permeating vapour is removed by means of a vacuum pump. It is easily understood that such a system is applicable when the volume of permeating vapour is relatively small, or the permeate side pressure is not too low. Otherwise vacuum pumps of extremely large capacities are required and the pumps will consume too much energy. After recompression the vapour may be condensed at the downstream side of the pump, this will always be necessary when emission control regulations have to be observed.

b. The permeated vapour is condensed at sufficiently low temperatures. This is the most cost effective way to maintain the partial vapour pressure at the permeate side at the required low value. Condensation temperatures may be reached simply with cooling water, in some application cooling media with temperature as low as –20° C are required. At these very low temperatures, however, the amount of permeate to be condensed is relatively small, and the cooling power required still economically acceptable. As the condenser surface will be installed at a certain distance from the permeate side of the membrane all non-condensable gases have to be removed from the permeate compartment in order to minimise any resistance for the transport of the permeate vapour to the condenser surface and any pressure losses. The composition of the permeate and/or the condensation temperature has to be adjusted that no freezing of the permeate will occur.

c. The permeate side of the membrane is swept with an inert gas in which the partial vapour pressure of the critical (preferential permeating) component is kept sufficiently lower than that on the feed side. This procedure is often discussed in the respective literature but not yet really introduced into practical application (with the exemption of air drying by means of membranes where part of the produced dry air is used as a sweeping gas). Otherwise the inert sweeping gas stream has to be preconditioned and, when laden with the permeated vapour, can usually not be wasted but has to be reconditioned and recycled. Reconditioning is generally done by condensation of the permeated vapour out of the sweep gas stream at sufficiently low temperature, followed by reheating in order to reduce the relative humidity and increase the capacity of the sweep gas stream. If a low partial vapour pressure has to be reached, the relative capacity of the inert gas stream will always be low, and large gas volumes have to be used. This is uneconomically compared to direct condensation. When normal composite membranes with a porous substructure are used only diffusive transport from the permeate side of the separating layer through the pores will occur, forming an additional transport resistance and reducing the total flux through the membrane.

In nearly all industrial pervaporation and vapour permeation installations the permeate is therefore directly condensed under vacuum. Depending on the nature of the organic components in the feed, which partially pass through the membrane, together with the preferential permeating component, depending on the final concentration to be reached in the product, and depending on the selectivity of the membrane condensation temperatures for large installations may vary between approximately +10 to

–20° C. When the required condensation temperature drops below the value of –20 °C recompression in a large vacuum pump (Fig. 3.3a) and condensation at atmospheric pressure will often be the better alternative.

Calculation of the required condenser surface is not trivial. In contrast to the common applications a superheated vapour mixture has to be condensed. For design calculations the selection of appropriate heat transfer coefficients has to consider the presence of non-condensable gases, partial condensation of the components along the respective dew lines under low pressure, the desired total condensation of the vapour in order to avoid loss of permeate through the vacuum pump, and the solubility of the components in the liquid phase.

Pressure losses caused by hydrodynamic resistance in the permeate pass will be detrimental to pervaporation processes. When an alcohol – water mixture has to be dehydrated to a final water content of 1 000 ppm even at 100° C the partial water vapour pressure at the feed side will be in the order of 10 mbar. Using a high selective membrane the partial water vapour pressure at the permeate side of the membrane will have to be kept at a few millibar. As this pressure is determined by the temperature of the condensing liquid permeate there has to be an unobstructed flow of the permeate vapour from the membrane to the condenser. It is obvious that even a pressure drop of one or two millibar will have a severe effect on the performance of the system.

From the above considerations it is evident that the operation parameters of an installation are closely related to the selectivity of the membrane. The latter has to be high at high concentrations of the component to be removed from the feed. When very low concentrations (e. g. below 1000 ppm) have to be reached in the retentate high selectivity is no longer desirable. At lower selectivity the partial vapour pressure of the critical component in the vapour passing through the membrane is reduced, leading to higher total pressures at the permeate side. Even if the permeate then contains more of the retained component than of the transported one its absolute amount is sufficiently small and high recovery ratios of the wanted, highly purified component will be obtained. With membranes which allow for an increase of the concentration of the retained component in the permeate with decreasing concentration of that component in the feed any final purity of the product can be obtained, e. g. water concentrations in ethanol as low as 10 ppm.

Condensation of the permeate below 0° C in dehydration application is only possible when the freezing point of the water is reduced by a portion of the (water miscible) organic component permeating through the membrane.

3.2.4 Principles of pervaporation

In Fig. 3.4 a principal scheme of a pervaporation process is shown. The liquid feed mixture is heated to the highest temperature compatible with its own stability, the stability of the membrane and all other parts (e. g. gaskets) in the system. All partial vapour pressures are at saturation and fixed by temperature and composition of the liquid mixture,

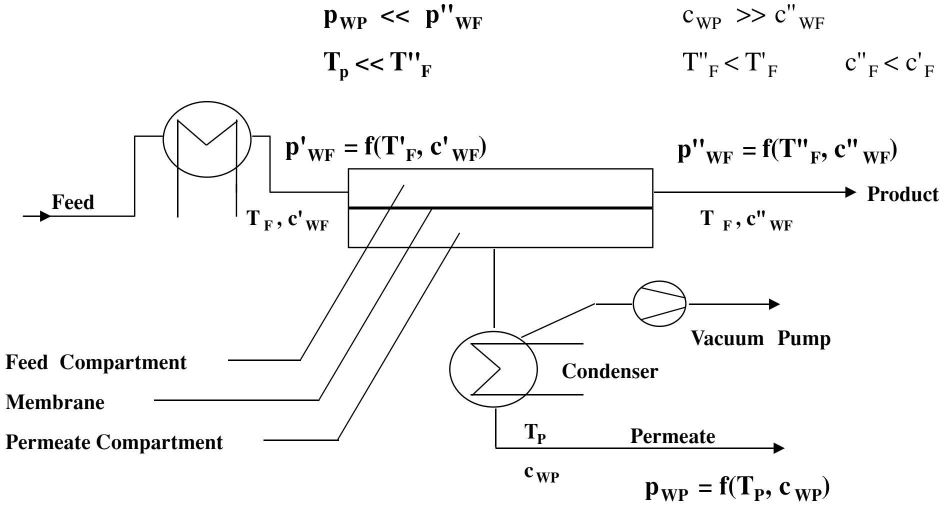

Fig. 3.4: Basic principle of pervaporation.

and by the nature of the components. On the permeate side all non condensable gases are removed by means of a vacuum pump, and the permeated vapours are condensed at a sufficiently low temperature. As the liquid feed mixture flows over the membrane and the better permeable component is removed and its concentration lowered, the heat for the evaporation of the permeate is passing through the membrane, too. The only source for this evaporation enthalpy is the sensible heat of the liquid. Thus a drop in concentration and in temperature occurs between the entrance of the feed on the membrane and its exit (Fig. 3.5).

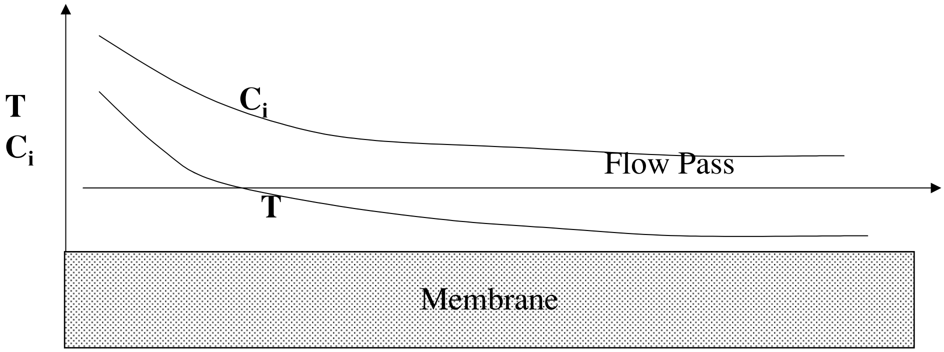

Fig. 3.5: Depletion of temperature and concentration along pervaporation flow pass.

This drop in temperature has several consequences. The partial vapour pressure of the critical (better permeating) component is decreased not only by the reduction of its concentration, but also by the reduction in temperature. Furthermore, as the diffusional transport through the membrane is temperature dependent an additional reduction of the transmembrane flux results. Whereas the flux drops approximately linearly with the reduction in concentration and the concentration drop is unavoidable (it is the goal of the process), the flux is reduced exponentially with the decrease in temperature. The membrane therefore does not operate at the temperature at which the feed firsts gets in contact with it but at a lower mean temperature (Fig. 3.6). More membrane area than for operation at constant temperature is required and a maximum limit for the temperature drop has to be found.

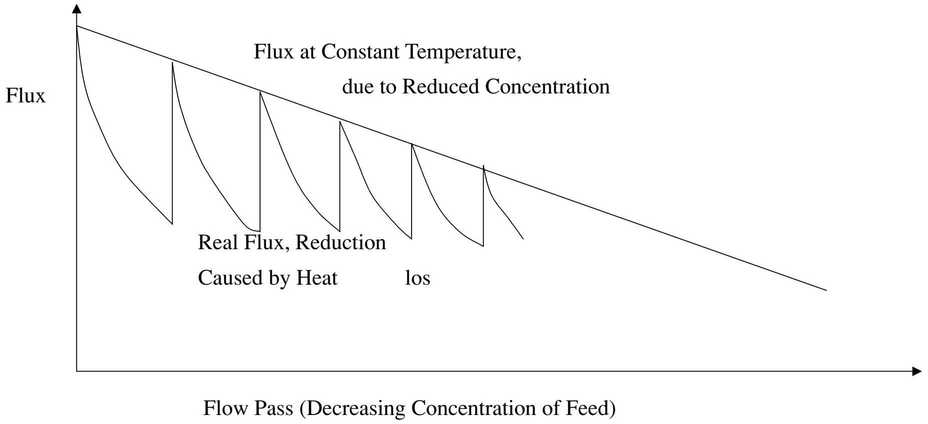

Fig. 3.6: Isothermal and real flux in pervaporation.

Different means have been proposed to overcome the effects of this heat loss: Direct heating of the membrane from the permeate side by steam, electrical heating of the membrane support, or heating of the liquid flowing over the membrane by an additional heat exchanger are just some examples. For practical applications only an arrangement as shown in Fig. 3.7 has proven to be useful. The total membrane area required for a specific separation is split into several so-called stages which are arranged in series, with an intermediate heat exchanger between each two stages. After passing over the membrane of the first stage, the lost heat is replaced in the intermediate heat exchanger before the feed gets in contact with the membrane area of the next stage. Total number of stages and size of each of the stages, and tolerated temperature drop per stage are matters of optimisation for the respective application and plant. Usually all stages will have the same membrane area and the size of the intermediate heat exchangers are adapted to the temperature loss per stage, but constant sizes of heat exchangers and adapted sizes of the stages have been verified as well. By a pressure control valve the liquid feed is

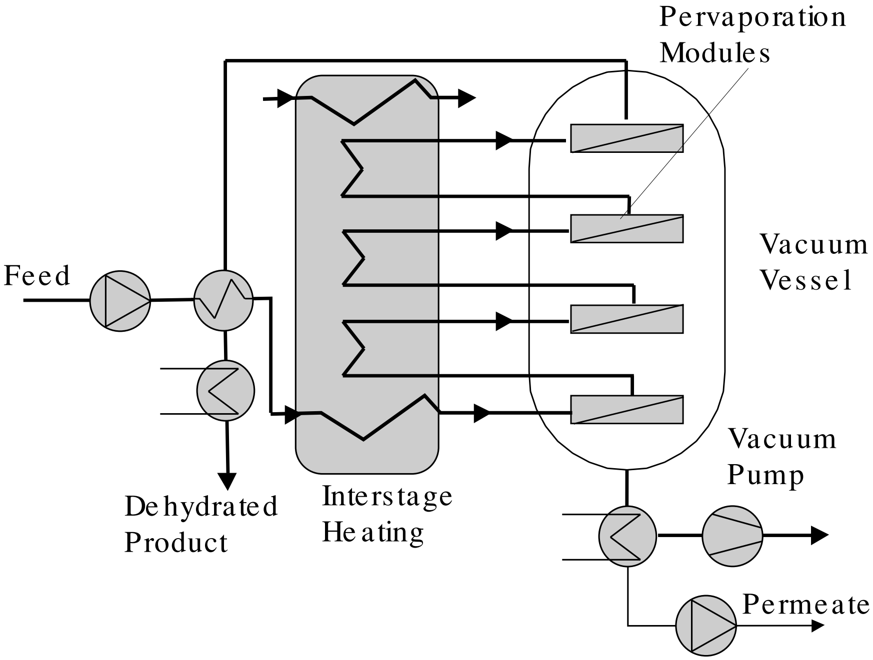

Fig. 3.7: Continuous pervaporation.

kept under pressure when the operation temperature is higher than the atmospheric boiling temperature.

For large plants each with a large membrane area optimisation will lead to a larger number of stages and in order to minimise the overall membrane area. Hydraulic pressure losses caused by too many stages and heat exchangers in series may be a important factor in the design of a large pervaporation plant. If the plant capacity is small and the concentration change large one would rather waste some membrane area and allow a higher temperature drop per stage, and thus reduce the number of stages, heat exchanger and the respective piping.

It is evident that the arrangement as shown in Fig. 3.7 reduces the energy consumption to a minimum. Only the heat required for the evaporation of the permeate has to be supplied and is lost in the process, the sensible heat of the product can be recovered to any extend, limited only by the costs for the interchanger.

As the loss of heat and the temperature reduction occur inside the membrane or at the permeate side the heat has to be transported by heat conduction through at least part of the membrane. The feed side surface will then be at a lower temperature than the bulk of the liquid flowing over it. Not only matter but also energy has to be transported through the boundary layer adjacent to the membrane surface. Whereas the difference in concentration of the better permeable component between the bulk of the feed and the membrane surface is a common phenomenon in all cross-flow membrane processes and known as “concentration polarisation”, the additional heat transport to and through the membrane is unique for pervaporation. Following the term “concentration polarisation” this effect is referred to as “heat polarisation” or “temperature polarisation”. Polarisation effects are the more pronounced the higher the flux through the membrane will be.

There is a certain difference in the concentration polarisation effects between the different membrane processes. In micro- or ultrafiltration or Reverse Osmosis, the major component from the feed is passing through the membrane and the minor component is rejected. This leads to a high increase in the relative concentration of this minor component in the boundary layer adjacent to the membrane, whereas the relative concentration of the major components changes to a small extend only. Back-diffusion of the minor component into the bulk of the liquid is therefore the more important factor, not the transport of the major component to the membrane.

In a pervaporation process, however, the minor component is passing through the membrane and the major component is rejected. Here small absolute changes of the concentration of the minor component in the boundary layer cause large relative changes, whereas the relative change in the concentration of the major component is small and often negligible. Therefore, the diffusive transport of the (better permeable) minor component from the bulk of the fluid to the membrane surface through the boundary layer is more responsible for the concentration polarisation phenomenon, than the back diffusion of the rejected major component. As long as the concentration in the feed mixture of this minor component to be removed is high, relative concentration changes are still small and concentration polarisation is not severe. It becomes a problem when the concentration of the better permeable component is low , and the diffusion of the better permeable component through the boundary layer will eventually determine the overall rate of the pervaporation process. The more high flux membranes are developed, however, the more attention has to be focussed to this polarisation problem.

In contrast to the aforesaid, heat polarisation is most severe at the high concentration of the component to be removed. Here fluxes of matter and of heat are the highest and the temperature drop is very fast. The temperature directly at the membrane surface will be much lower than in the bulk of the liquid and thus the membrane is operating at a much lower temperature than it is indicated from measurements in the bulk of the feed. High Reynolds numbers and high mass flow rates at the feed side are means to counteract temperature polarisation. At low feed concentrations, on the other side, heat polarisation is less important, as the amount of evaporating permeate will be small.

Both polarisation effects can in principle at least be partially reduced by the same means as in other membrane processes, by high Reynolds numbers at the membrane surface and frequent remixing of the feed stream. An appropriate design and calculation of the module into which the membrane is incorporated, taking into account the differences between pervaporation and the other membrane processes is essential. Hydrodynamic pressure losses in the feed, and energy costs for pumping will limit the applicability of high Reynolds numbers.

3.2.5 Principles of vapour permeation

Vapour Permeation differs from pervaporation, as stated above, insofar as the liquid feed to be separated is pre-evaporated and a vapour phase gets directly in contact with the membrane surface. At least the better permeable component is kept as close to saturation conditions as possible. Thermodynamically there is no difference between a liquid and the its equilibrium vapour, the partial vapour pressure and thus the driving force for the transport through the membrane are identical and the same "Solution-Diffusion-Mechanism" is valid. The heat for the total evaporation can usually be recovered only partially (for pre-heating of the feed), thus the energy lost in a vapour permeation application is higher than by using the liquid feed stream directly. As the feed mixture getting in contact with the membrane is already in the vapour phase no phase change occurs across the membrane and thus no temperature polarisation will be observed. Concentration polarisation, however, is still an issue. Although the diffusion coefficient is much higher in a vapour than in a liquid, this is at least partially outbalanced by the lower density of the vapour, and therefore concentration polarisation effects may be observed at low concentrations of the component to be removed.

Today vapour permeation processes are widely used in the dehydration of organic solvents, or in the removal of methanol from other organic components, or in the removal of VOC's from gas streams. In the literature the term "vapour permeation" is often related to the removal of organic vapours ("VOC's") from air or gas streams only. In these applications the better permeable component is brought close to saturation by cooling, compression, or both pre-treatment steps. Thus there is no real reason for such a narrow definition and the means by which the vapour has been produced has no influence on the choice or nature of the membrane nor the mechanism of the separation process.

A principle scheme of a vapour permeation plant is shown in Fig. 3.8. The liquid feed mixture to be separated is preheated and totally evaporated, the saturated vapour is fed to the membrane system. The whole membrane area is arranged in one stage, and will in general operate at the same temperature. Intermediate heat exchanges with the respective temperature controls and the interconnecting piping are no longer required. By means of a pressure controller the vapour is kept under constant pressure. Recovery of the heat of evaporation from the product is possible in principle, but usually not economic, except that part required to preheat the liquid feed to boiling temperature.

The evaporator may be part of the plant, in many applications the saturated vapour comes from the top of an upstream distillation column. Thus a vapour permeation step may be coupled with one or more distillation columns in a so called hybrid system.

As can be see from comparison of Fig. 3.7 and 3.8 the permeate side arrangement remains unchanged and the same for both variants, as thermodynamically these are identical processes.

Superheating of the vapour should be strictly avoided. When a vapour is superheated the partial pressures of its components are not increased, at low degrees of superheating the vapour in contact with the membrane will behave as if it were supplied at the

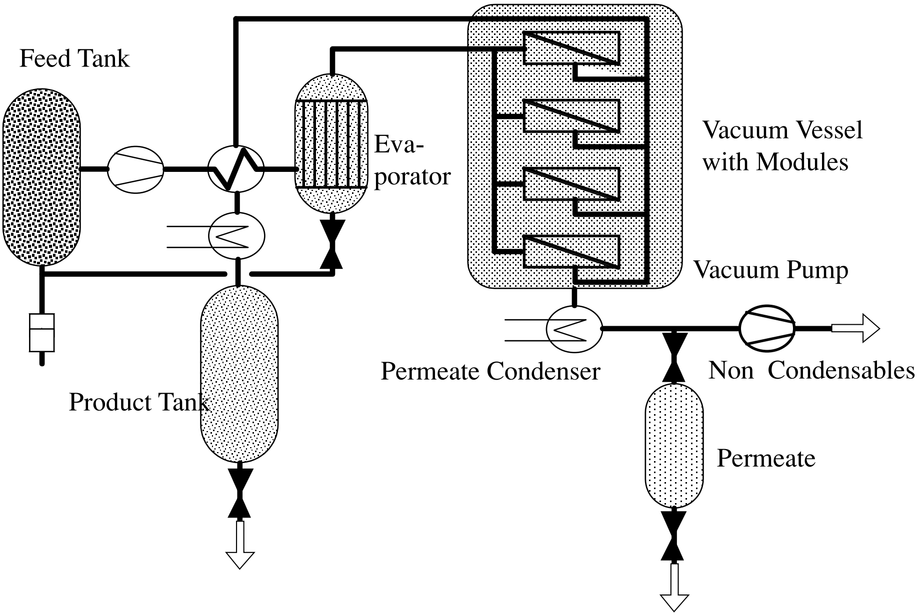

Fig. 3.8: Principle of a vapour permeation unit.

respective lower saturation temperature. Larger degrees of superheating will result in a drop of the performance of the membrane even below the values observed at the equivalent saturation temperature, as the activity coefficients (or fugacity coefficients) will drop. Furthermore with increasing superheating the density of the vapour decreases and less molecules get in contact with the membrane per unit of time. This effect will result in a flux reduction, too.

When saturated vapour is fed to the membrane it is unavoidable that a small portion of the vapour will condense on the membrane. This will happen during start up of the installation when the first vapour reaches the still cold membrane and module, and during shut-down, respectively. Additionally some heat will always be lost to the outside of the modules during operation.

Besides these heat losses effected more by the physical arrangement of the installation, there are two more, caused by the laws of thermodynamics:

1. The vapour is expanded from the high pressure at the feed side to the low pressure at the permeate side. This will cause a Joule-Thompson effect, which in general will lead to a slight temperature drop from the feed to the permeate side and cool the membrane. Although this effect will reduce the temperature by one to three degrees centigrade for most of the mixtures treated in practical application, it will lead to condensation of a small part of the vaporous feed.
2. In most applications the composition of the feed mixture will be at or close to a minimum boiling point azeotrope. By removing one of the components from the mixtu-

re (e. g. water in a dehydration process) the boiling point of the mixture will increase as shown in Fig. 3.9 for the system n-propanol – water at atmosperic pressure. When water is removed from the vaporous mixture at azeotropic concentration the boiling temperature increases and at constant pressure (at which a vapour permeation plant will be operated) the mixture is moved into a region of oversaturation, where only liquid can exist. Consequently part of the vapour has to condense and liquid and vapour will exist in equilibrium. The heat freed by the partial condensation will increase the temperature of the system to the new equilibrium value. The respective compositions of vapour and liquid are given by the horizontal connection between the dew point and the bubble at that temperature. Therefore, if a mixture is fed at a composition equivalent to a minimum boiling point azeotrope to a vapour permeation plant the vapour will increase its temperature when passing over the membrane, and leave the system eventually at the boiling temperature of the pure organic component. This effect is negligible in the dehydration of azeotropic ethanol where the difference between the boiling point of the azeotrope and that of the pure alcohol is only a few tenth of a degree. In the example of the system water – n-propanol of Fig. 3.9 this temperature can be as high as 10° C., and the effect is even higher for other systems.

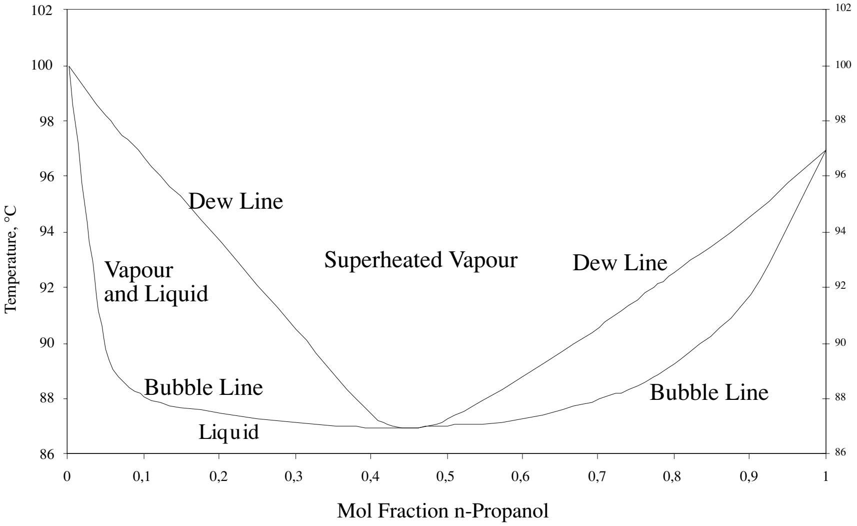

Fig. 3.9: Dew and bubble point of water-n-propanol.

As usually identical membranes are employed for both liquid and vaporous feed mixtures the partial condensation of vapour on the membrane in vapour permeation will have no detrimental effect on the performance of the membrane nor the process. It could even be proven that the highest performance can be obtained with the same membrane, when a mixture of liquid and vapour is directly used as a feed [27]. Condensation of the vaporous portion supplies the heat necessary for the evaporation of the permeate and thus temperature polarisation is avoided. As the volume of the vapour phase will exceed that of the liquid a strong mixing effect will occur at the membrane surface, reducing concentration polarisation, too.

The choice whether to apply the liquid feed mixture directly to the membrane in a pervaporation process or pre-evaporate it and feed a vapour to the membrane, depends mainly on specific site conditions.

Vapour permeation is preferred when:

- the feed is already available in the vapour phase, e. g. from a distillation column at the specified temperature (e. g. 95 to 105° C),
- dissolved or undissolved solids are present in the original feed (e.g. the feed is a mother liquor), and an additional purification step by evaporation has to be performed anyway,
- the plant capacity is small but a large concentration change has been specified which otherwise would request too many small stages
- the additional heat consumption of the plant is not an issue.

Vapour permeation offers the advantage of:

- simple plant arrangement, all membrane area in one stage,
- no need for intermediate heat exchangers, the interconnecting piping, and controls
- no heat polarisation occurs as the evaporation enthalpy has already been supplied to the feed
- the total membrane area is operated at a higher temperature, and less membrane area is required,
- polluted feed streams, containing impurities, can be processed in one plant.

3.3 Membranes

The development of membranes for pervaporation and vapour permeation was highly influenced by the development of desalination and gas separation membranes and the theoretical knowledge of membrane structure and transport through membranes gained thereby. First tests with pervaporation in the late seventieth and early eightieth were even performed using membrane originally developed for reverse osmosis. It was, however, fairly soon understood that, despite the similarities, both processes require different membranes. In both processes the transport through the membrane is a diffusional one, the dense layer responsible for the separation has to be as thin as possible. In desalination high pressures are applied, up to 100 bar at ambient temperatures, whereas is pervaporation pressure differences across the membrane are in the range of a few bar only. On the other side pervaporation membranes have to be stable against aggressive organic components at temperatures of 100° C and above. In reverse osmosis both sides of the membrane are in contact with a liquid phase and the degree of swelling between the two sides does not differ too much. In pervaporation the feed side of the membrane is highly swollen in contact with the hot liquid (or saturated vapour), whereas the permeate side is "dry" and virtually non-swollen. A high gradient of swelling thus exists over the separating layer of the membrane, demanding additional resistance and stability. It is thus not surprising that specific membranes, made from different materials had to be developed, although the general structure of pervaporation membranes and those for reverse osmosis are very similar.

Two different types of pervaporation membranes based on polymeric materials were developed at about the same time in the beginning of the eighties:

- Hydrophilic membranes, with a preferential permeation for water, utilised mainly for the removal of water from organic solvents and solvent mixtures, with an emphasis on azeotropic mixtures. Membranes for the removal of small alcohol molecules like methanol and/or ethanol are of hydrophilic nature as well.
- Organophilic membranes with a preferential permeation for non-polar compounds, utilised for the removal of volatile organic components from aqueous and gas streams.

In both applications a composite membrane structure (Fig. 3.10) is preferred, allowing for very thin defect free separation layers, but with sufficient chemical, mechanical, and thermal stability. Due to the composite structure flat sheet configurations are preferred, too. The substructure of both types of flat sheet pervaporation membranes is very similar: A porous support membrane with an asymmetric pore structure is laid onto a carrier layer of a woven or non-woven textile fabric and a basic ultrafiltration membrane is formed. On the free side of this asymmetric porous substructure the pores have diameters in the order of 20 to 50 nanometers which widen up to the fabric side to the micrometer range. Polyester, polyethylene, polypropylene, polyphenylene sulfide, polytetrafluor ethylene, and similar fibres are used for the textile carrier layer. Structural polymers with high resistance against chemical attack and good thermal and mechanical properties like polyacrylonitrile, polyetherimide, polysulfone, polyethersulfone, and polyvinylidenflu-

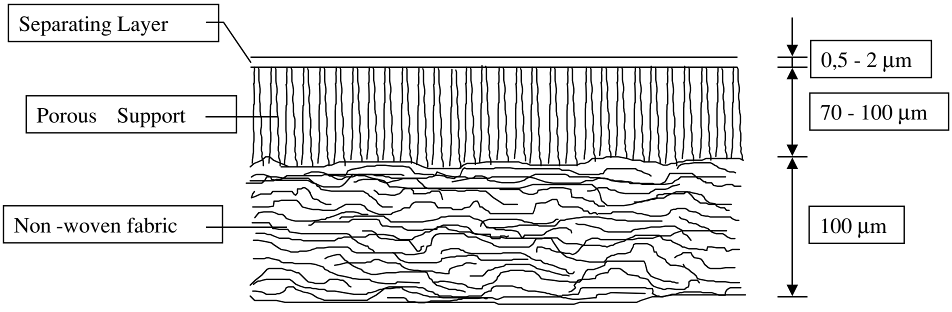

Fig. 3.10: Cross-section of a composite membrane.

oride form the porous support. All these structural polymers have already a certain intrinsic separation characteristic, they generally have a high permeability for polar substances like water.

On this substructure a thin dense layer (in the range of 0.5 to 10 µ thick) is coated which has a very good separation capability. Different coating techniques are in use, most commonly a solution of the respective polymer in an appropriate solvent is spread onto the porous substructure. The solvent is evaporated, followed by further treatment to effect crosslinking of the polymer. Photosensitive, solvent-free prepolymers may be used for coating which later are cross-linked by irradiation, e. g. with UV-light or electrons.

The dense defect-free separating layer of hydrophilic membranes is made from different polymers which have a high affinity towards water. These polymers contain ions, oxygen functions like hydroxyl-, ester-, ether-, or carboxylic moieties, or nitrogen as imino- or imido- groups. They must be cross-linked in order to render them insoluble after the coating process. Preferred hydrophilic polymers are polyvinylalcohol (PVA) [28], polyimides, natural polymers like chitosan blended with other polymers [29], or cellulose acetate (CA), or alginates, which are cross-linked by various chemical reactions. Other techniques are the deposition of thin layers from a vapour by means of cold plasmas where at least one of the gaseous components contains the above mentioned groups [30]. Ion exchange polymers have been used as well, either with sulfonic or carboxylic acid groups , the latter mainly in the salt form with an alkali ion as the counter ion [31]. Polyelectrolytes formed by blending and internal neutralisation of an anion and a cation exchange polymer are reported in literature, too [32].

Organophilic membranes have the same structure as hydrophilic ones. The dense separating layer is formed by cross-linked silicones, mostly polydimethyl siloxane (PDMS) or polymethyl octyl siloxane (POMS). The methods to apply the dense layer on the porous substructure are similar to those used for hydrophilic membranes.

If instead of flat sheets tubular membranes are manufactured, it is very difficult to coat a dense, defect free, but very thin layer on such a structure. A lot of effort has been devoted to the development of hollow fibre membranes, however, so far only organophilic ones are available with a composite structure, as for organophilic membranes the dense separating layer should not be too thin. Hydrophilic hollow fibre membranes are produced with dense symmetric walls, without any further structure. As these walls are comparably thick, in the order of several ten micron, specific fluxes of the membrane are very low, so their advantages over flat sheet membranes are not very high.

In more recent developments inorganic separation layers are applied, either by coating the porous substructure with a layer of zeolites [33], or by reducing the size of the pore to molecular dimensions by deposition of amorphous silica [34].

Zeolites are alumiumsilicates with a broad range of the aluminium to silicium ratio. They form crystalline structures with well defined pores in the range of several Angstrom. At high aluminium to silicium ratio the crystal and especially the inner lumen of the pore is hydrophilic with a preferential sorption of water inside the pores. At low aluminium content the zeolites are organophilic with preferential sorption of organicsin the pores.

Again a composite structure has been chosen comprising a porous support, made from ceramics or stainless steel. Several layers of the zeolites are coated on the porous substructure until all defects between the crystals in one layer are covered by crystals of another layer. Separation through these membranes is effected by adsorption of the better permeable component (water) inside and transport through very small pores, the size of which is in the order of the size of a water molecule (three to four Å). Zeolites as the effective moiety in the separating layer offer the advantage of uniform pore size, as the diameter of the pore inside a zeolite crystal is fixed by the nature of the zeolite. Especially NaA-type zeolites are extremely hydrophilic and the pore of the crystal is accessible for water molecules only. High selectivity and high fluxes are reported for hydrophilic zeolite membranes, they shall be stable at temperatures of at least 150° C. The more hydrophilic the zeolite, however, the higher is the sensitivity against acidic conditions, Especially NaA-type zeolites are immediately destroyed when they get in contact with acids. More acid stable zeolites are less hydrophilic, thus the selectivity and the flux of the respective membrane is substantially lower when used in dehydration applications.. First pilot scale modules are available.

Coatings of amorphous silica can be applied by a sol-gel technique or through interfacial precipitation. As the surface of the amorphous silica contains hydroxyl groups, the separating layer is highly hydrophilic, too. Amorphous silica is stable against acid conditions. It is, however, difficult to obtain a uniform pore size by simple coating, therefore a multilayer structure is found in this type of membranes as well. The diameter of the coarse pores of the substrate is first reduced by coating with aluminium oxide before the final layer of amorphous silica is applied. Selectivity and flux of silica membrane is comparable to that of a zeolite membrane.

Following first test reports fluxes and selectivities are comparable to those reported for zeolite membranes, temperature stability is even higher, up to 250° C. Again first laboratory and pilot plant scale module are offered and under testing.

The separation mechanism of inorganic membranes is even more complex than that of polymeric separating layers. Compared with polymeric pervaporation membrane these inorganic ones are not dense, but porous. Molecular sieving effects, caused by shape and size of molecules, and shape and size of the pores are first determining the separation. The surface of the membrane and the inside of the pore wall are highly hydrophilic, so preferential sorption of water on the membrane and inside the pores and surface diffusion in the adsorbed layer play an additional very important role.

Organophilic zeolite membranes have been tested in the laboratory. An application is expected for the removal of methanol and ethanol from larger organic molecules like ethers and esters. On the surface of the amorphous silica membranes other functional moieties can be grafted to the free hydroxyl groups at the surface. By such grafting the affinity of the surface to molecules can be changed and the development of organophilic membranes seems feasible.

Inorganic membrane are so far mostly manufactured as tubes, with the separating layer on the inside or outside surface of the tube. They are resistant against temperatures up to 250° C, and against all neutral organic solvents, especially aprotic ones, like DMF, NMP, DMSO. The inorganic layer does not swell, they will be therefore less sensitive against fast concentration and temperature changes than the polymeric membranes. Acid and alkali resistance of the silica membranes have not yet been fully tested, but are probably comparable to those of the best polymeric membranes.

Up to today inorganic membranes are by far more expensive than polymeric ones. This is due to the higher cost of the substructure, a sintered ceramic or stainless steel tube, and to the multi-layer coating procedure, requiring usually a high temperature heat treatment between two coating steps. Module assembly with connections between ceramic tubes and the stainless steel of the other module components is complicated and expensive, too. At least partially these higher costs are outbalanced by the higher flux of inorganic membranes, compared to polymeric ones, especially when operation at higher temperatures is feasible. It is therefore assumed that, like in other membrane processes, polymeric and inorganic membranes will find their respective areas of applications.

Zeolites are widely used in separation of purely organic mixture in adsorption processes. It remains a challenge to membranologists to develop new membranes with such zeolites forming the separating layer for future organic – organic separation.

3.3.1 Characterisation of membranes

The performance of a membrane is in general characterised by its flux and its selectivity. For practical reasons fluxes for pervaporation membranes are just given in either kg/m^2 h or in Mol/m^2 h, either as total flux of all components or separated into the partial fluxes of the different components. As the flux depends on the composition of the feed for hydrophilic membranes the concentration of the water in the feed of the respective measured value has to be indicated, too. For comparison of different membranes very often the so-called "Pure Water Flux" is calculated by dividing the actual flux by the water concentration of the feed (see J_0 in equation 7) As stated above the "Pure Water Flux" is depending exponentially on temperature.

$$J_0 = J_c / c_{Feed} \tag{26}$$

Selectivitiy is indicated in different ways. Most commonly found in literature is the co-called α-value. This is calculated as the ratio of the better permeable component (water) to the lesser permeable component (organic) in the permeate divided by the respective ratio in the feed.

$$\alpha = \frac{(c_{water} / c_{org})_{Permeate}}{(c_{water} / c_{org})_{Feed}} \tag{27}$$

Although the α-value looks fairly simple it is not very informative. For most dehydration membranes the composition of the permeate is constant over a very broad range of feed compositions. As a consequence the a-value is not a constant but varies considerably, depending to which feed composition it is related.

Secondly membrane selectivity is characterised by the so-called b-value or enrichment factor. This is simply the concentration of water in the permeate divided by that in the feed.

$$\beta = C_{wp}/C_{wf} \tag{28}$$

or

$$\alpha = \beta\, C_{of}/\, C_{op} \tag{29}$$

Again this numerical value is informative for only one feed concentration and not very useful if different membranes have to be compared.

Therefore it has become quite common to drop numerical values of the selectivity. Instead of that the composition of the permeate is plotted in a diagram over the water content of the feed (Fig. 3.11 for ethanol-water, Fig. 3.12 for acetonitrile-water) similar to the well known McCabe-Thiele diagram in distillation and use such diagram for comparison of different membranes.

For organophilic membranes the separation layer is formed mostly from siloxanes like polydimethyl siloxane (PDMS), or polyoctylmethyl siloxane (POMS). These separating layers are usually thicker than those for hydrophilic membranes.

Again flat sheet membranes dominate the applications, but hollow fibres and capillary membranes are in use, too.

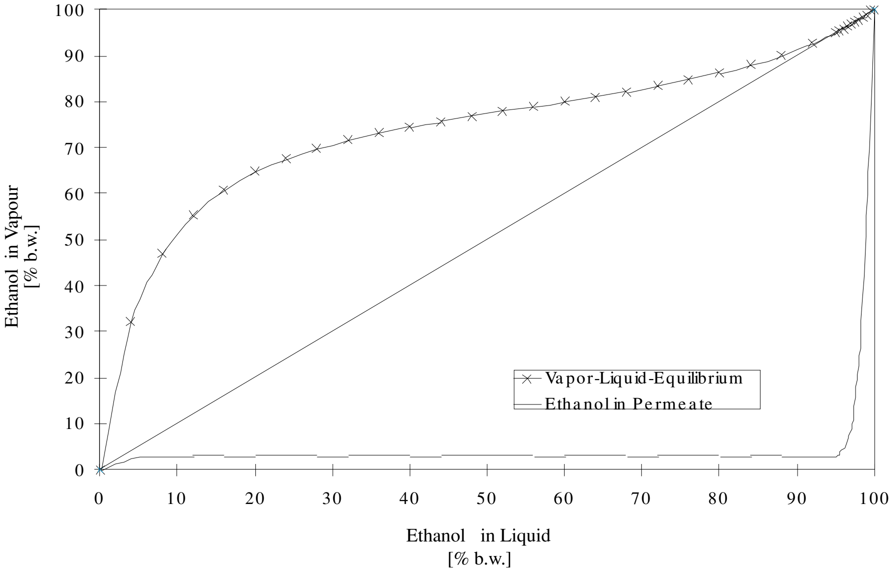

Fig. 3.11: Ethanol-water; VLE vs . pervaporation, PVA-PAN membrane PERVAP® 2200.

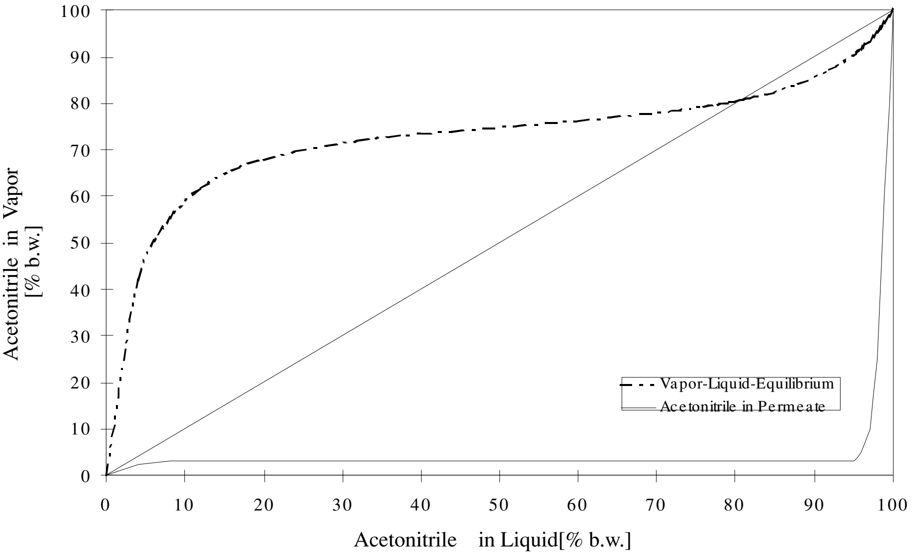

Fig. 3.12: Acetonitrile-water ; VLE vs. pervaporation, PVA-PAN membrane PERVAP® 2201.

Fluxes of organophilic membrane are defined in the same way as for hydrophilic membranes. However, when applied in the removal of low concentrations of volatile organics from water, the flux of the latter can be regarded as constant at constant temperature, as the concentration of water in the feed remains nearly unchanged. Consequently selectivity will vary in the same range. Fluxes of the volatile organic component is highly depend on the nature of the component and may differ by orders of magnitude for different components. For the low concentrations of the organic substance a linear relation between flux of the component and its concentration in the describes the process with sufficient accuracy. b values or enrichment factors are used for the characterisation of membrane performance.

In the past years knew efforts have been made in academia and industry to develop new membranes for organic-organic separation. Of specific interest are the separation of olefins from paraffins, e. g. propene from propane, aromatics like benzene or toluene from aliphatic hydrocarbons or the separation of the xylene isomers. A number of different membranes are reported in the patent literature, but so far no industrialisation could be achieved. The only industrial processes in this area are the separation of the light alcohols methanol and ethanol from their mixtures with hydrocarbons, ethers, and esters. The membranes in use are, however, still of the hydrophilic type, in which the more polar small alcohols replace the water [15, 35].

So far only polymeric membranes are applied in pervaporation and vapour permeation processes. Thermal, mechanical, and chemical stability of the porous substructure as well as of the textile fabric are limiting factors for the operation range of this type of membrane, more than the stability of the separating layer. Demand for higher operation temperatures and chemical resistance have stimulated the development of inorganic substructures, preferentially porous ceramics. These can be coated by cross-linked polymeric separating layers similar to those on polymeric substructures, however, then the chemical stability of the organic component will limit stability and application.

3.4 Modules

Design of modules for pervaporation and vapour permeation processes had been based on the experience gained in those for water treatment by membranes, like Ultrafiltration and Reverse Osmosis. However, significant modifications had to be made due to the specific requirements of pervaporation and vapour permeation processes. Whereas in the water treatment the portion of the feed volume passing into the permeate is small, in pervaporation and vapour permeation the volume of the permeate is much larger than that of the feed.

Pressure losses at the feed side have to be reduced to a minimum in vapour permeation. Otherwise the process would no longer operate at constant pressure, but the feed vapour could reach a region where superheated conditions would exist. Consequently pressure losses in vapour permeation modules have to be as low as several millibar only.

In pervaporation feed side pressure losses are not that important, but in multistage arrangements will eventually limit the number of applicable stages.

The partial vapour pressure at the permeate side has to be reduced in both processes to fairly low values, especially when low final concentrations of the critical component have to be reached in the retentate. Therefore any pressure losses, even in the range of a few millibar have to be avoided at the permeate side.

As any feed mixture will contain organic components at high concentration, mostly at elevated temperatures, chemical and mechanical stability of all module components, like spacer, gaskets, potting material and glues is critical. So far mainly four different types of modules are in use on an industrial scale.

3.4.1 Plate modules

Plate modules are mainly used for dehydration applications, with permeate channels as open as applicable. A rectangular support plate is provided on both sides with gaskets, which partially cover slots in the plate, acting as distribution channels. On each gasket a membrane is placed, its feed side facing the plate. The permeate side of each membrane is supported by a perforated plate, between two perforated plates a grid or spacer is placed. A membrane, one side of the support plate, and a gasket form a feed chamber, two perforated plates and the space between them a permeate chamber. Each feed chamber is thus adjacent to a permeate chamber, each permeate chamber has a feed chamber at each side. Alternatingly feed and permeate chambers are arranged in a module.

The module package ise held together by means of flanges and bolts. Thickness and weight of bolts and flanges limits the maximum internal pressure for such modules to 6 to 10 bar. In order to keep weight and handability and weight of the modules within a reasonable range, the maximum size of these modules does not exceed 30 to 40 m^2 of membrane area or less than 100 support plates.

Stainless steel is used as a construction material for support plates for the membranes and for spacers. Chemically stable elastomers, like EPDM or perfluorinated polymers are used as gasket material, more widely used is expanded graphite, due to its excellent chemical and thermal resistance. Preferentially the permeate channels are open over the circumference of the module which are assembled inside special vacuum vessel. Intermediate heat exchangers and the permeate condenser are sometimes installed inside the vacuum vessel, mostly these items are installed outside for easier access and maintenance.

Usually all membranes in a module are arranged for parallel flow of the feed. The feed channel, between membrane and supporting plate, has a height between 0.5 to 1 mm, linear flow rates are in the order of cm per minute. Serial flow would be desirable in order to allow for higher linear flow velocities and higher Reynolds numbers, but then feed side pressure losses will become too high.

Alternative designs are very similar to plate heat exchangers, in which the supported membrane replaces the heat exchanger plates. These modules may be open or closed to the outside at the permeate side, with internal ducts for feed and retentate, and, when closed, for permeate removal. It has been proposed to integrate plate heat exchangers as preheater and permeate condenser into such modules.

3.4.2 Spiral wound modules

Spiral wound modules with stainless steel central tubes, but otherwise similar to those known from the conventional membrane processes ultrafiltration or Reverse Osmosis, are in use, mainly for organophilic membranes. Due to the larger molecular weight of the substances removed through organophilic membranes the volume of the vaporous permeate is much smaller, even at the same permeate side pressure, and the total permeate side pressure can be usually higher than in dehydration applications. Thus pressure losses in the permeate channels are less critical than in water removal. As organophilic applications operate at lower temperatures and low concentrations of organic solvents in the feed, polymers materials can be used as spacer or glue. One or several of the spiral wound modules are housed inside a pressure tube and assembled in conventional skids, very similar as in water treatment.

Similar consideration are valid for organic – organic separation. Spiral wound modules have thus bee used in pilot plants for the removal of methanol and ethanol from dry organic mixtures or for the removal of aromatic from aliphatic components. Stability of the material for the feed side spacer and the glue are problems still to be solved.

There has been a development on spiral wound modules for dehydration applications, too. So far this did not lead to applications in industrial plants. Chemical stability problems of the components and too high pressure losses in the permeate side spacer could not be solved satisfactorily, and the costs of the modules and for the installation in a plant were not really lower than those for plate modules.

3.4.3 Envelope module

A special module design which is a hybrid between a plate module and a spiral module has been developed by the research institute GKSS in Germany. Here two membrane sheets are welded together (by heat or ultrasonic welding) to a sandwich structure with a permeate spacer between the two membranes. A multitude of these sandwiches, each with a central hole are arranged on a central perforated tube which removes the permeate. Each membrane sandwich is sealed from the feed to the permeate side by means of a gasket. Around the central hole a perforated ring is inserted into the permeate spacer in order to have an unhindered flow of the permeate into the permeate tube. Feed spacer keep the membrane sandwiches apart from each other. Feed flow over all sandwiches in a module can be in parallel, by means of additional separation plates any number of the sandwiches can be arranged in groups, with the flow parallel in each group, but in serial for the groups. The central tube with the membrane sandwiches around is housed inside a feed vessel, usually of stainless steel. Originally these modules were developed for water treatment, but are now widely used with organophilic membranes in the recovery of organic vapours especially gasoline vapours from gas streams.

3.4.4 Tubular modules

As stated above, inorganic (ceramic) membranes are produced mainly as tubes. The obvious module is therefore a tube bundle very similar to a tubular heat exchanger. The detailed arrangement depends on the fact whether the separating layer of the membrane is on the inside or on the outside of the tube.

In the first case a bundle of membrane tubes is connected on both ends into tube sheets, each individual tube sealed and fixed. The feed is more or less evenly distributes and directed into the inner lumen of the tubes. Well defined flow regimes and high Reynolds numbers can be obtained at the feed side, controlling polarisation effects like in water treatment application. Depending on the inner diameter of the tube the ratio of feed volume to membrane surface is rather high, and the feed stream cannot be heated inside the module. At high linear velocities this may require partial recirculation of the feed or very small modules in series with the respective intermediate heat exchangers. The permeate flow from the outside surface of the tubes is not obstructed, the permeate vapour can be condensed inside the module shell which has to be kept under vacuum. Sealing of the ceramic tubes to the metal tube sheets and the different thermal expansion of metal and ceramic in the module are problematic.

In the second case, with the separating layer on the outside of the tube, the tubes need to be fixed on one side only to a tube sheet only, On this side the inner lumen of the tubes is open to the permeate volume. Baffle plates are required over he outside of the tube bundle in order to achieve good flow distributions and high Reynolds numbers in the feed. The flow regime is not that well defined as in the first case and maldistribution and dead ends may occur. Heating of the feed in the module through additional heat exchanger tubes or through the shell of the module is feasible. The flow through the membrane and the inner diameter of the tubes limit the length of the module, as otherwise the pressure drop at the open permeate side will become too high.

In a more recent development each tubular membrane is again fixed and sealed to a tube sheet, with the inner lumen on one side open to the permeate compartment. Additionally each membranes tube is housed inside a heat exchanger tube. The feed flows through the annulus gap formed by the outside surface of the membrane and the inner surface of the heat exchanger tube (Fig. 3.13). The feed volume per surface area of membrane can now be controlled by adjusting the height of the annular gap. High linear velocities and thus very high Reynolds numbers can be achieved by this arrangement, without too high volume to surface ratios. From the outside of the heat exchanger tube the feed can be directly heated and the heat lost by the evaporation of the permeate reintroduced. By specific means the direction of the feed flow can be reversed at the end of

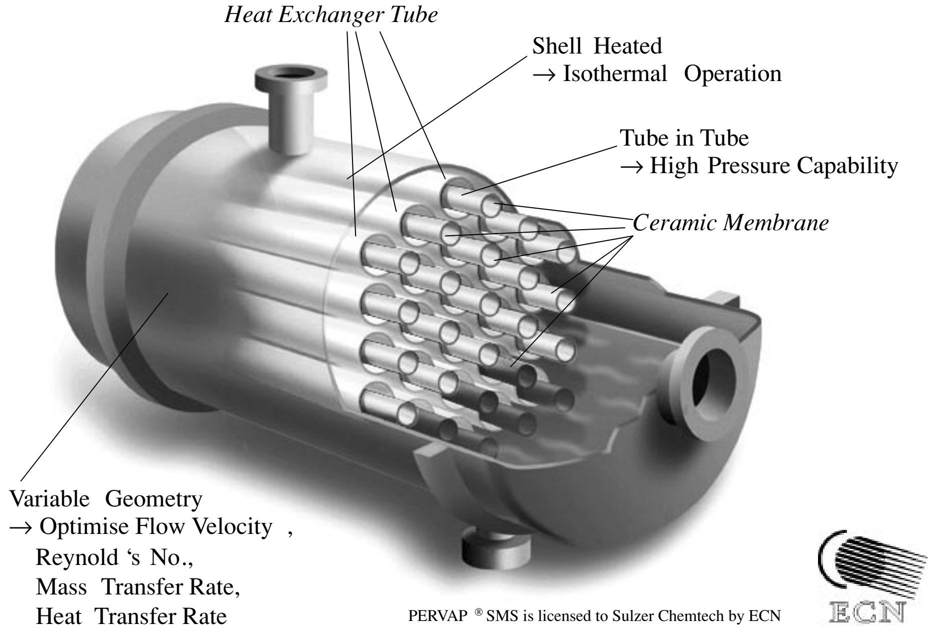

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Fig. 3.13: Isothermal module.

the annular gap, and the membranes can be arranged for serial or parallel feed flow, or any combination thereof.

3.4.5 Other modules

Hollow fibres or capillary modules have not yet found an industrial application in pervaporation or vapour permeation processes. A few data have been reported were organic capillary structures with an outside diameter of 0.5 to 1 mm have been coated with silicon and used in organophilic separation. With the flow on the shell side permeate pressure losses inside the bore of the fibre control the process. For specific organophilic applications, these pressure losses may be tolerable. For hydrophilic applications the modules, however, even at an inner diameter of the capillary of 1 mm the useful length of a module would be in the order of 20 to 30 cm only. Such a module, including housing and connection in any industrial application, is more costly than a plate module.

So far no potting material is available which combines the necessary chemical and mechanical stability at the operation temperature and pressure of a dehydration plant.

Microfibres with an inner diameter of 20 µ and a wall thickness of 10 to 20 µ have been proposed, too. Specific flux through such a homogeneous membrane would be low, but outbalanced by high packing density and low membrane costs. Fibre length would be in the order of 20 cm, arranged in a modified module, in which the fibres would be potted in axial direction into the wall of a tube. So far no reports are known on any application of such a module.

3.5 Applications

3.5.1 Organophilic membranes

Organophilic membranes are mostly applied for the removal of volatile organic components (“VOC’s”) from gas stream like waste air or nitrogen. Main applications are the treatment of streams originating from the evaporation of solvents in coating processes in the film and tape production, the purge of products like polymers, by which unreacted monomers are removed, or from breathing of storage tanks for solvents and especially from loading and unloading of gasoline tanks in tank farms. In many installation the feed stream received at atmospheric pressure is compressed in order to increase the feed side partial vapour pressure of the component to be removed to or above saturation level. Partial condensation of the critical component before entering onto the membrane is a wanted side effect. The permeate is enriched in the critical component, but not necessarily to saturation. It is compressed by means of a vacuum pump and led to the inlet of the feed compressor. The condensate obtained between compressor and membrane is than the only outlet for the separated and recovered organic. In specific cases compression at the feed side is sufficiently high to avoid the application of a vacuum at the permeate side.

The economy of the process is usually determined by the value of the recovered substances. Emission regulations in all industrial countries demand for very low final concentrations if the gas stream is released to the atmosphere, therefore the retentate from the gas purification by the membrane is either recycled to the upstream process or further treated by an additional polishing step.

Although considerable effort in research and development has been devoted to the removal of VOC's from aqueous streams this technique has not yet been introduced into the industry. Potential mixtures like waster water streams which could be treated are more complex, the economical value of the recovered substances is low. Even when a pure substance like phenol can be efficiently removed and recovered from water competing processes like biological treatment or adsorption are cheaper and better introduced. Applications may be found in the future in biotechnological processes where high value products can be separated from a fermentation broth and can be concentrated and purified in the same step.

3.5.2 Hydrophilic membranes

The largest industrial installations of pervaporation and vapour permeation processes are equipped with hydrophilic membranes and used for the removal of water from organic solvents and solvent mixtures.

3.5.2.1 Solvent dehydration

Pervaporation

Although the first pervaporation plants were installed for the dehydration of bio-ethanol, already in 1985 a first plant for dehydration of ethylacetate started its operation in the chemical industry. The first plants were still isolated, that is working from a storage feed tank to a product storage tank (see Fig. 3.7). With relative small capacities of a few tons of solvent per day they could easily by-passed if any problems would occur. With increasing experience and confidence in the new technology, quite soon solvent dehydration by means of pervaporation and vapour permeation became an essential step in a production. Today the technology is regarded as a reliable process and, in numerous applications, is even an integrated part of a production process.

Organic solvents are used for a variety of purposes in the chemical industry e.g. for synthesis of pharmaceuticals, to precipitate materials from aqueous solutions, for cleaning purposes and for drying of final products.

Spent solvents nearly always contain some water. Dehydration is an essential step in their recovery but difficult since most of the more common solvents form azeotropes with water. Final water removal by distillation is then impossible or complicated. Conventional entrainer distillation is not a real option for pharmaceutical or fine chemical production. The addition and afterwards removal of the entrainer is difficult and the residual concentration will have to be monitored continuously. Furthermore, entrainer distillation systems require a certain minimum capacity to be economical. Quite often this capacity is above the amount of solvent which will have to be treated at a single location. The only solution is then in many cases to ship out the spent solvent and buy fresh one, with all the related problems of logistics and storage.

Pervaporation eliminates the need of an entrainer. It is regarded as a physical process, thus its validation is not too difficult. Due to its modular nature a pervaporation plant is economical even at small capacities, which can be increased by the addition of more membrane area. A well designed and operated pervaporation plant will recover 90 to 97 % of the solvent contained in a feed mixture, thus reducing storage and shipping of hazardous goods. On site solvent recovery using pervaporation and vapour permeation is becoming standard practice in the pharmaceutical and chemical industries.

The most important solvents to be treated are the light alkohols, ethanol, the propanols, and butanols. Methanol is rarely treated by pervaporation as it does not form an azeotrope with water and can easily be purified by distillation. Selectivity and flux of the polymeric membranes are generally not in favour for the dehydration of methanol. Other solvents are esters like ethyl- and butylacetate, ketones like acetone, butanone (MEK) or methyl isobutyl ketone, ethers like tetrahydrofurane (THF) or methyl tertiary butyl ether, or acetonitrile, or mixtures of these solvents. The final water concentrations to be reached vary between 1 % to below 500 ppm for the alcohols to below 100 ppm for THF.

The installed plants are either of the type as shown in Fig. 3.7 or batch plants as shown in Fig. 3.14. In the first case the plant and the number of stages is optimised for a specific separation and capacity, and consumes the minimum of energy. If a different stream has to be treated, the plant will be operated outside optimal conditions, and compromises with respect to capacity or final product quality will have to be accepted.

In a batch plant there is usually only one stage and preheater. The feed stream is circulated back to the storage tank and passed over the membrane several times until the whole content of the tank has reached the final specification. Due to the lower efficiency caused by the unavoidable redilution of the product and the fact that not all the sensible heat of the circulating stream can be recovered, such plant consumes more energy and requires more membrane area than the straight forward plant of Fig. 3.6. However, it offers more flexibility with respect to the final product quality by additional passes of the feed. Capacity can be adapted by the same means, and streams of different nature and composition can be treated with the same plant. Equation (21) is a useful tool in estimating plant capacity and product quality, when the pure water flux of the installed membrane is known for different feed streams.

Vapour Permeation

The criteria to choose between pervaporation or vapour permeation have been discussed in chapter 3.2.5. In Fig. 3.8 the principal features of a stand-alone vapour permeation plant are shown. The liquid feed stream from a storage tank is completely evapo-

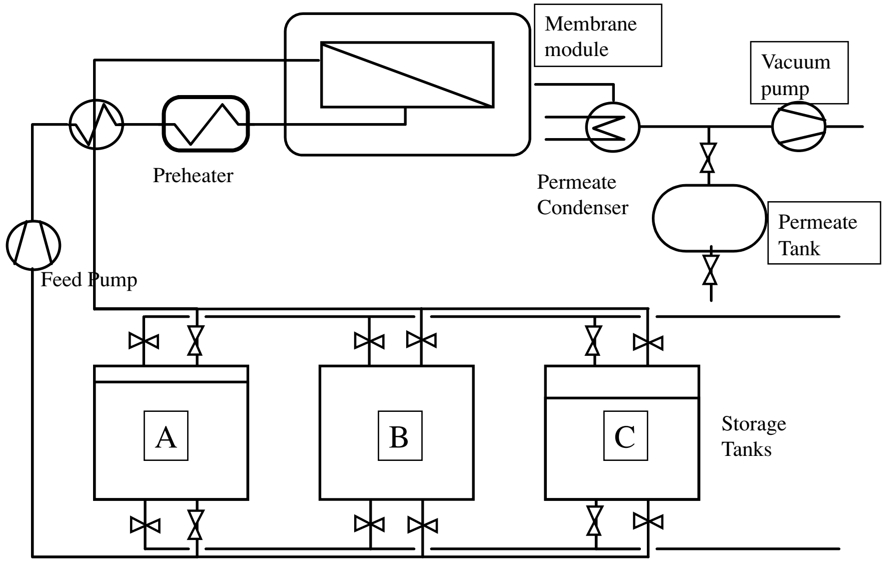

Fig. 3.14: Pervaporation – batch plant.

rated, the composition of the vapour entering upon the membrane equals that of the feed. If the feed is an azeotrope the composition of liquid feed, vapour, and evaporator content are identical. If the feed is not an azeotrope the composition of the evaporator content will vary from the two other streams. Depending on the concentration of the impurities and their solubility in the liquid in the evaporator a bleed stream will have to be removed from the evaporator. In specific applications, e.g. treating a mother liquor, this bleed stream may be as high as 10 % of the total feed. It was found that even from fairly pure solvents, e.g. in the electronic industry, low volatile impurities accumulate in the evaporator, necessitating to drain the evaporator every couple of weeks.

The coupling of a distillation column with a vapour permeation plant, the latter treating the azeotropic vapour from the top of the column is shown in Fig. 3.15. The distillation column may have to be operated under pressure in order to allow the membrane system to be run at a temperature of around 100° C. The permeate can be recycled to the inlet of the distillation column, which will result in nearly 100 % recovery of the organic component. The only additional energy input in this scheme for the final dehydration of the azeotrope is for the condensation of the permeate, as the dehydrated product would have to be condensed anyway. Optimisation between the concentration of the vapour entering the membrane system and thus between the size and energy consumption of the column on one side and the size of the membrane system

In specific cases when the vapour-liquid-equilibrium favours distillation at the side of the organic component of the azeotrope and a high purity of the organic is specified, a hybrid system as shown in Fig 3.16 may be economically advantageous. Here the membrane system is used to cross the azeotropic point, the partially dehydrated vapour

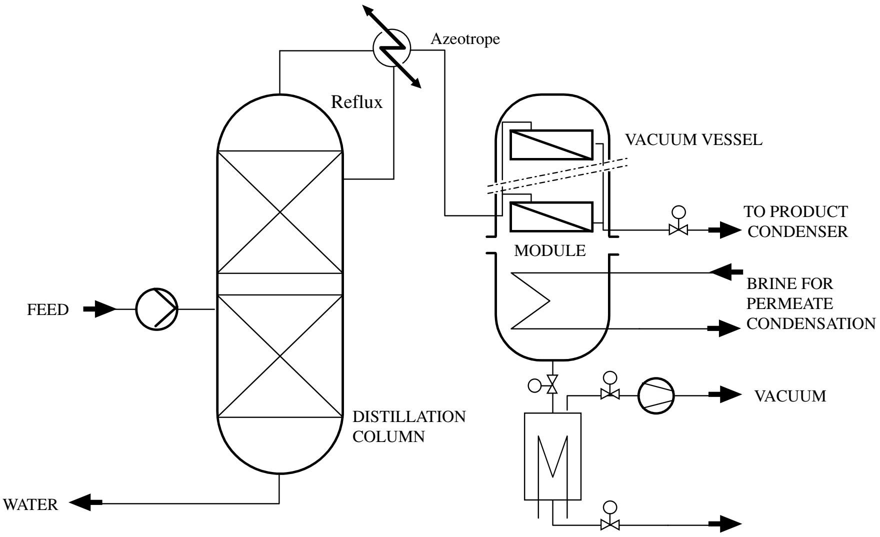

Fig. 3.15: Vapour Permeation coupled with Distillation

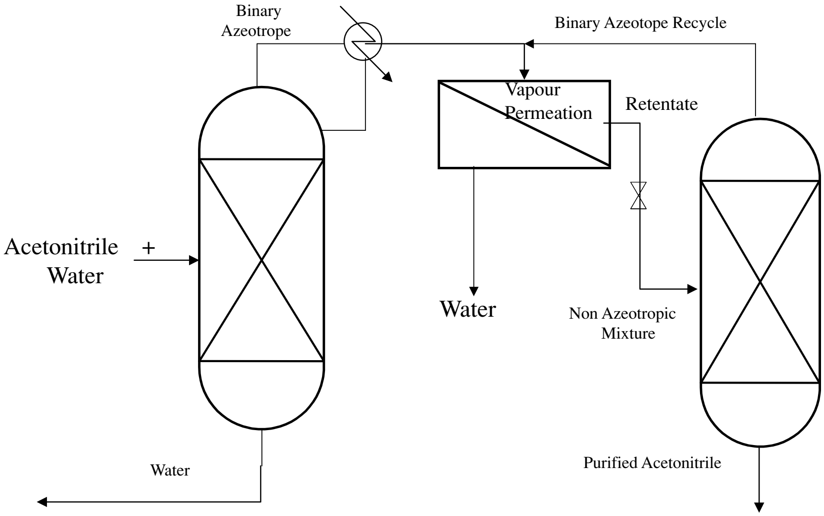

Fig. 3.16: Azeotrope splitting between two columns.

enters the second column in which final dehydration is effected. Again it is necessary to determine the economical optimum between the size of both columns, the energy consumption of the first one and the volume of the recycle stream from the second column at one side, and the size of the membrane system and its outlet concentration.

Figure 3.17 depicts a similar arrangement, however, here two organic components, an alcohol and an ester have to be separated and purified from their ternary mixture with

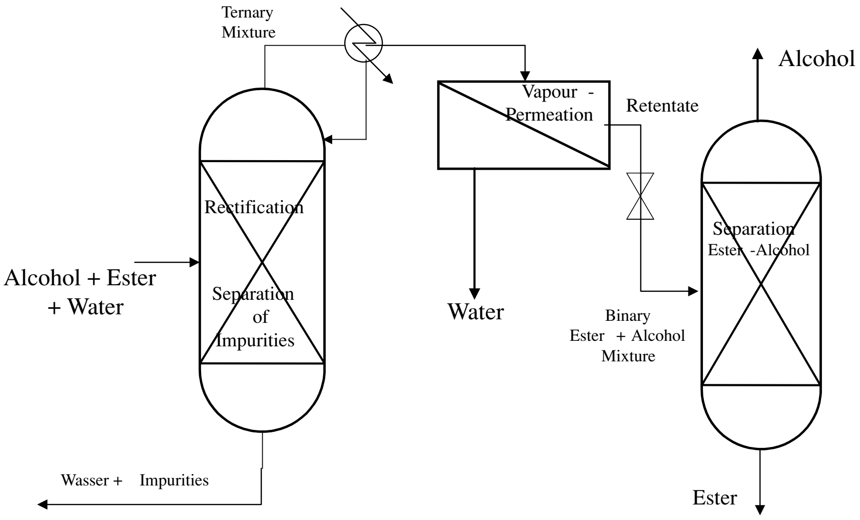

Fig. 3.17: Hybrid system for the separation of a ternary mixture.

water. The ternary vapour mixture from the first column is passed over the membrane of the vapour permeation unit, and nearly all water is removed. The permeate is recycled to the inlet of the first column. The two organic components can now be separated in the second column, which any residual water leaving together with the alcohol.

When the original feed composition is on the organic side of the azeotrope an arrangement as in Fig. 3.18 may have its advantages. The column separates the feed into the high boiling organic at the bottom and a low boiling mixture close to the azeotrope at the top. This vapour from the top is passed through a vapour permeation plant which removes water, preferentially to a residual concentration close to that of the original feed. This retentate is recycled to the inlet of the column. All the water from the feed has to permeate through the membrane, but the most economical concentration range can be chosen. A certain drawback of this arrangement is the fact that any impurities of the original feed will remain in the purified organic stream.

Existing azeotropic distillation plants for the dewatering of organic solvents can simply be revamped by the addition of a vapour permeation or pervaporation unit. Such plants comprise usually a first distillation column by which the feed is distilled close to the binary aqueous – organic azeotrope. In a second column the entrainer is added, which forms a ternary azeotrope with water and the organic. At the bottom of the second the column the dry organic component is obtained, whereas the ternary azeotrope from the top of this column is condensed and split into two phases, an aqueous one, which is fed to a third column for further purification and entrainer recovery, and an organic one, which is returned to the second column. The upper part of this second column is limiting the capacity of the plant as all water has to pass through it as the ternary azeotrope. When the stream from the first column is increased, the additional water can be removed by a pervaporation – vapour permeation system, without overloading the second

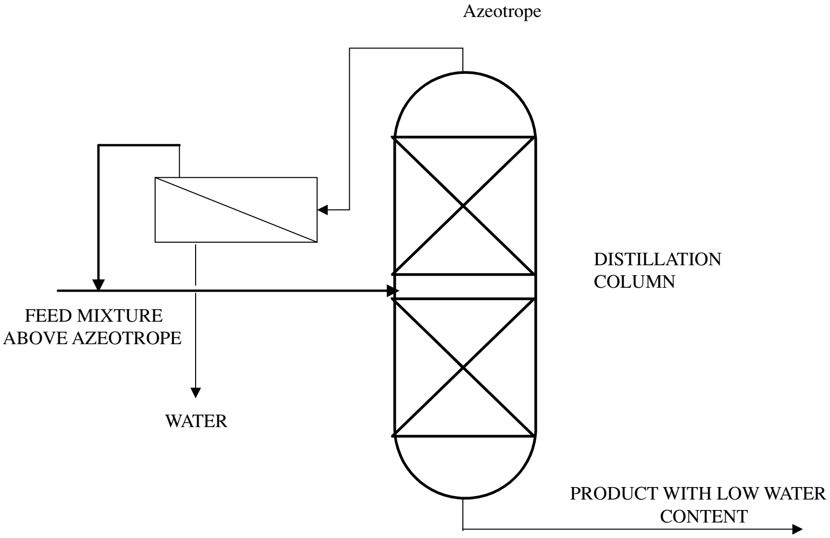

Fig. 3.18: Hybrid process – feed above azeotrope.

column. Calculations have proven that the capacity of an existing azeotropic distillation can be increased by up to 40 % by reducing the reflux ratio of the first column and removal of the excess water by pervaporation.

Any of the commonly used chemical engineering programs (Aspen®, Chemcad®, PROII®) can be used for calculation and simulation of these hybrid system. An additional modulus has to be introduced into the program which in rather simple terms describes the membrane system. Even a modified version of equation (21), relating feed flow and concentration, product flow and concentration, and membrane area would be sufficient for a first design.

3.5.2.2 Removal of water from reaction mixtures

In many chemical reactions like esterification, acetalisation, ketalisation, or etherification water is produced as an unwanted by-product. As all these are equilibrium reactions of the form

$$A + B \Leftrightarrow C + H_2O \tag{30}$$

Removal of the water from the mixture will shift the reaction equilibrium to the side of the wanted product. If one of the educts is used at a surplus over the stoichiometry nearly full conversion of the other, usually the more valuable educt can be achieved. This will result in a much higher yield of the wanted product. Furthermore, the wanted product has no longer to be separated and purified from a four component mixture (the two educts, the wanted product, and water), but from a two component mixture. Water has been removed through the pervaporation membrane, one of the educts nearly totally converted, thus the product has to be separated from the surplus educt only. This facilitated downstream purification may be even at least as economically important as the higher yield and conversion ratio.

The most simple arrangement of a pervaporation system coupled to a reactor is schematically shown in Fig. 3.19. A batch reactor is filled with the reaction mixture, one of the educts at precalculated stoichiometric surplus. The mixture is passed continuously over the pervaporation membrane, until the water introduced with the raw materials and freed in the reaction has been removed to the wanted extend. As indicated in Fig. 3.19 the more volatile portion, e.g. an aqueous azeotrope can be alternatively evaporated from the reactor and passed through a vapour permeation unit. By arranging several reactors and membrane systems in a cascade and passing a bleed stream downstream of the first membrane system to a second reactor, a continuous operation is possible. Depending on the type and nature of the reaction reactors, membrane systems, and distillation columns can be combined in different arrangements for an optimum yield and downstream purification. One of the first industrial plants, combining pervaporation and an esterification reaction, operating continuously with a cascade of reactors and pervaporation units has been described in [36].

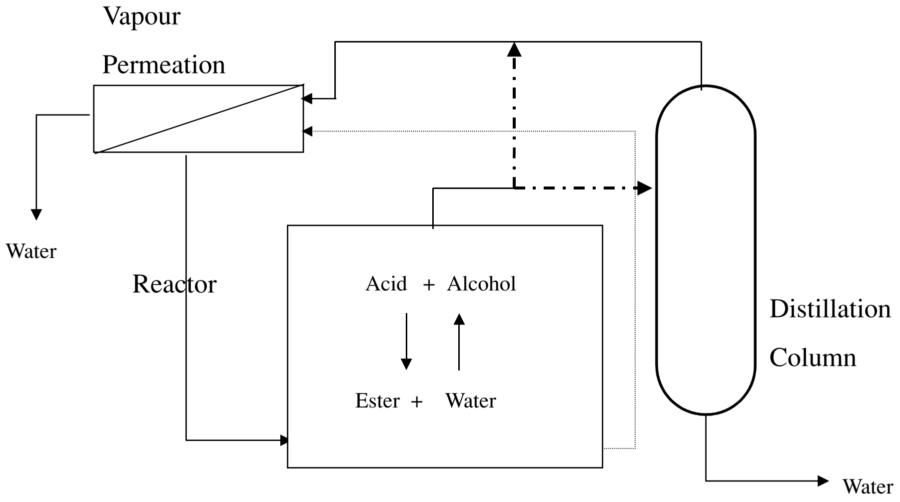

Fig. 3.19: Reaction, coupled with pervaporation/vapour permeation

For a simulation and optimisation for the coupled process the kinetic of the reaction and the performance of the membrane have to be known. A reaction as in equation (30) can be described by

$$dC/dt = k_1 [A] [B] - k_2 [C] [H_2O] \qquad (31)$$

The symbols in brackets relate to the concentration of the respective substances, k_1 and k_2 are the reaction rate constants for the forward (esterification) and backward (hydrolysis) reaction, including their dependence on temperature and catalyst activity. For a given reaction the equilibrium constant is then given

$$K = k_2 / k_1 \tag{32}$$

For the formation of water an equation similar to (31) is valid

$$dH_2O/dt = k_1\,[A]\,[B] - k_2\,[C]\,[H_2O] \tag{33}$$

When water is removed from the mixture The kinetic of water removal can be described as

$$- dH_2O/dt = [H_2O]\,P\,F/M \tag{34}$$

with F the membrane area, M the mass of the reaction mixture and P the permeability of the membrane. For simplicity is assumed that P depends on temperature only, not on any concentration. Introducing the water removal into eq. (33) one gets

$$dH_2O/dt = k_1\,[A]\,[B] - k_2\,[C]\,[H_2O] - [H_2O]\,P\,F/M \tag{35}$$

or, combining all constants in eq. (34)

$$dH_2O/dt = k_1\,[A]\,[B] - k_2\,[C]\,[H_2O] - [H_2O]\,D \tag{36}$$

Calculation of the increase of the product C is more tedious. The interdependent differential equations equations (32) and (35) have to be solved numerically, which with today's computer is not too difficult.

In Fig. 3.20 the conversion conversation ratio of the wanted product (ester) and the water present in the reaction mixture are plotted over the reaction time for a given membrane area and two ratios of the educts. The wanted product C and water are produced at the same rate, and both concentrations in the reaction mixture increase. As water is continuously removed through the membrane at a certain time the water content passes through a maximum, when the water is as fast removed as it is formed. The time to reach this point depends on the membrane area installed. The water content then goes down and reaches eventually a value close to zero, when the water is much faster removed than formed.

At the stoichiometric ratio of the educts the conversation ratio of component C only asymptotically approaches the 100 % value. This is easily understood from eq. (31). When virtually all the water has been removed from the mixture, the rate of formation of component C depends on the rate of the forward reaction only. As the concentrations of component A and B have become small, their product is even smaller, and the overall reac-

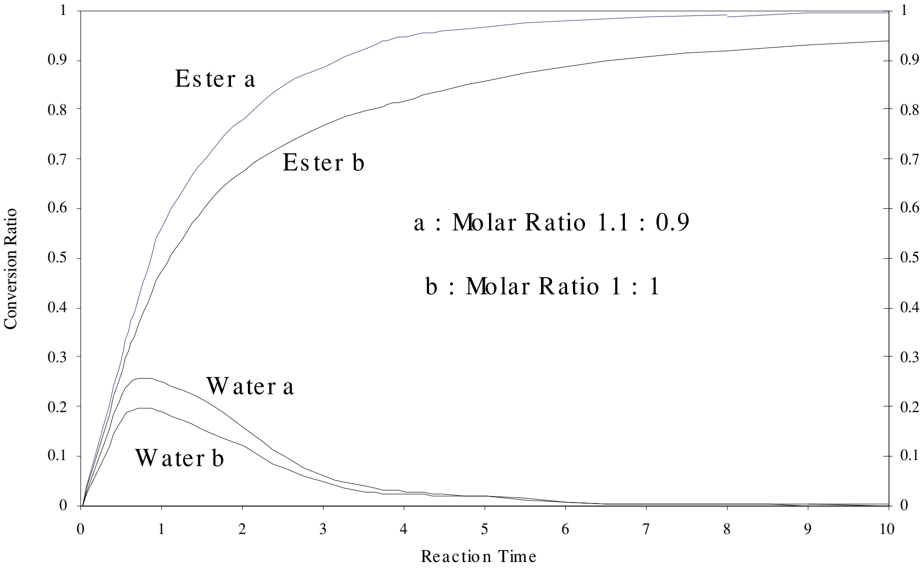

Fig. 3.20: Coupled reaction – pervaporation.

tion rate could only be improved by an increase in the reaction rate constant k_1, e.g. by increasing the reaction temperature or catalyst activity.

Starting at a non stoichiometric ratio of the educts, the concentration of the surplus educt is higher at the end of the reaction and remains nearly constant. The second order reaction of eq. (31) becomes then a first order reaction, and full conversion can be reached in definite time.

With the knowledge of the kinetic parameters for a given reaction which are relative easily accessible by a test or even found in the relevant literature, and the membrane performance the optimum ratio F/M of membrane area can be determined for that reaction, with the initial ratio of the educts as a adaptable parameter.

3.5.2.3 Organic-organic separation

As outlined in chapter 3 membranes for the separation of real organic-organic mixtures have still be to developed and introduced into industrial application. However, specific modification of hydrophilic membranes can be used to remove the light alcohols methanol and ethanol from their mixtures with other organics. The selectivity of these membranes is not that high as in dehydration processes, but sufficient for effective and economical large scale industrial applications. One such plant for the removal of methanol from an organic azeotrope is described in [30].

In the production of trimethyl borate (TMB) methanol and boric acid are fed to a reactor followed by a reactive distillation column (Fig. 3.21). Methanol is used in a surplus in order to convert all the boric acid and avoid the pollution of the bottom product

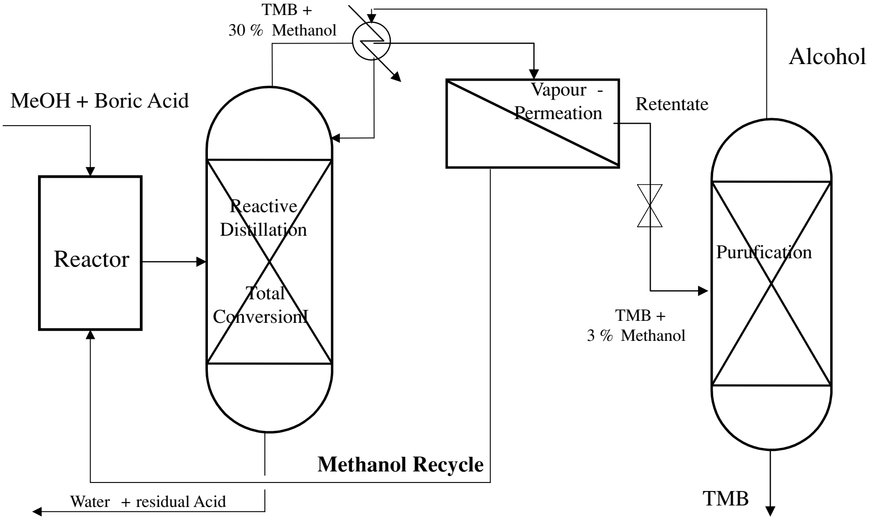

Fig. 3.21: Trimethylborate production with vapour permeation.

of the reactive distillation column with residual acid. From the top of this first column an azeotropic mixture of 30 % methanol and 70 % TMB is obtained under higher than atmospheric pressure. This azeotrope cannot be separated by water wash, as the TMB will immediately hydrolyse when in contact with water. The azeotropic vapour is thus led to a vapour permeation unit, equipped with membranes which permeate methanol, but retain TMB. The concentrated TMB, which contains about 3 % of methanol is introduced into a second distillation column, which separates the feed into pure TMB at the bottom and a nearly azeotropic mixture at the top. This mixture is returned into the reflux of the first column, the permeate of the membrane system, mainly methanol, is recycled to the reactor.

In their publication the operator states that the investment for the membrane system is lower than for a competing absorption system, combined with considerable savings in energy, personal and maintenance costs, resulting, as they say, in a negative pay-back period.

In additional plants methanol is separated from other methylesters of simple organic acids, which generally form azeotropes with methanol.

A specific application is found in transesterification reactions, where a methylester is reacted with another alcohol, e.g. one containing an amino group. It is desired to convert all of the alcohol, therefore a surplus of the methylester is applied. Again an azeotropic mixture of methanol and the respective methylester is obtained as a by-product. For recirculation of the ester the methanol content has to be reduced significantly, which can be effected by pervaporation.

In the production of methyl tertiary butylether (MTBE) and ethyl tertiary butylether (ETBE) a C4 cut, is reacted with a surplus of the respective alcohol to the ether. Only the isobutene is selectively converted. From the reaction mixture the unreacted C4 and the surplus of alcohol has to be separated. Unfortunately both ether form azeotropes with the respective alcohol, so their separation is effected by several distillation columns, operated at different pressures. When a side stream of the first debutanizer column (Fig. 3.22) is extracted and passed over a pervaporation membrane, the alcohol can be removed through the membrane and returned to the reactor. No significant residues of alcohol will then be present in neither the bottom nor the feed product. A more detailed engineering study [37] has shown that only a relatively small membrane area is required for a large scale production plant, combined with significant savings in operation costs.

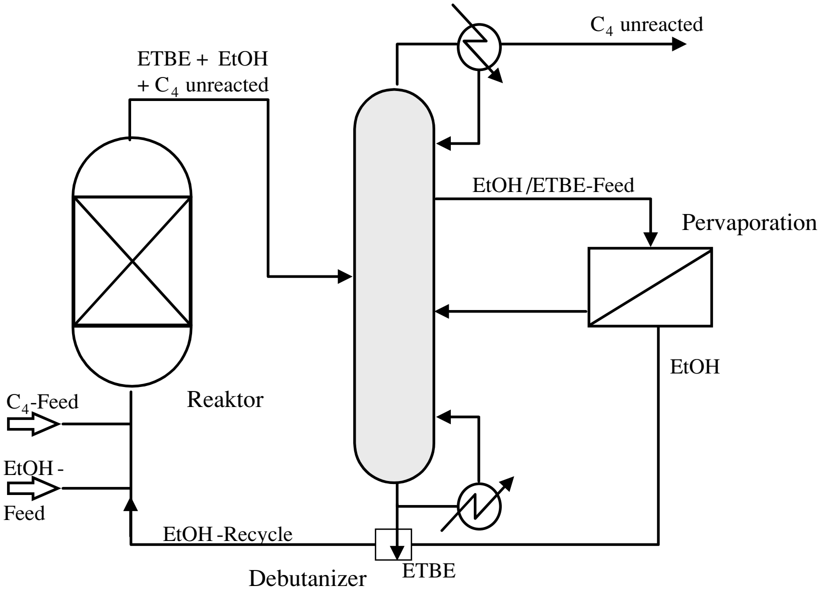

Fig. 3.22: Debutanizer with side stream.

3.6 Conclusion

During the past 15 years removal of water from organic liquids and liquid mixtures by means of pervaporation/vapour permeation has developed into a mature technology. More than 150 industrial plants have been installed around the world, with capacities between 20 kg/h to several tons per hour. Nearly all of these plants are equipped with polymeric membranes, which also are used in the plants for removal of methanol from its azeotropic mixtures. The introduction of ceramic membranes will not only enlarge the area of application of the process to higher temperature and aggressive mixtures, but also help to overcome the prejudice which some engineers still have against the application of polymer membranes.

Development of new membrane, probably more inorganic than organic one, may in the future even allow for real organic-organic separation.

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4 Nanofiltration of Charged Organic Molecules in Aqueous and Non-aqueous Solvents: Separation Results and Mechanisms

J. A. Hestekin, C. N. Smothers and D. Bhattacharyya

Nomenclature

a_s	ion size parameter
A	pure water permeability constant, m/(s*bar)
C_s	concentration of solute in the membrane, mol/m^3
C_w	concentration of water, mol/m^3
D_e	dielectric constant
D_s	solute diffusivity, m^2/s
D_w	diffusivity of water, m^2/s
F	Faraday's constant, (9.652x10^4 amp-s/g-equivalent)
I	molar concentration of the solvent, mol/m^3
J_w	water flux, m^3/m^{2}s
K_1	solute-pH rejection coefficient 1
K_2	solute-pH rejection coefficient 2
ΔP	pressure difference across membrane, bar
ΔpK_a	change in the pKa as a result of the solvent in the system
R	rejection of the solute
R_g	gas constant, (L*atm)/(mol*K)
R_p	pore radius, m
T	absolute temperature, K
$V_{\underline{i}}$	partial molar volume of the solvent, m^3/mol
V_w	partial molar volume of water, m^3/mol
z_i	valence of ion

Greek Letters

δ	solubility parameter, Mpa$^{1/2}$
δ_d	dispersive forces solubility parameter, MPa$^{1/2}$
δ_h	hydrogen bonding forces solubility parameter, MPa$^{1/2}$
δ_p	dipole-dipole forces solubility parameter, MPa$^{1/2}$
ε	membrane porosity

γ_i	activity coefficient
${}_s\gamma_i$	concentration activity coefficient
${}_m\gamma_i$	solvent medium activity coefficient
η	solution viscosity, Pa s
$\Delta\pi$	osmotic pressure difference across membrane, bar
ρ	density of solvent, kg/m^3
τ	membrane tortuosity
ψ	Donnan potential of the membrane

Abstract

Nanofiltration is a membrane separation with increasing industrial applications because of the possibility of selective separations. Although the transport through this membranes with aqueous systems has been studied extensively, the transport of organic solvents is much less understood. For these reasons, we have studied the use of highly hydrophilic, negatively charged nanofiltration membranes for the separation of ionized organic molecules from water and organic systems. This work has shown, in part, that the ionization of the organic molecule plays a big role in the rejection because of Donnan repulsion. We have shown an approach for estimating the separation via degree of ionization for water and alcohol systems. Finally, we have shown that the flux of organic solvents through hydrophilic nanofiltration membrane can be correlated with solubility parameters.

4.1 Introduction

Membrane processes have found wide applications for the treatment of aqueous based systems involving material recovery, reuse, and for pollution prevention. One of the most exciting membrane technologies is nanofiltration (NF) of the potential of selective separations at moderate pressures. NF membrane separation falls between reverse osmosis and ultrafiltration with a MW cut-off ranging anywhere from 200–1000 Daltons [1, 2, 3]. For membranes containing charged groups (such as, COO^-, SO_3^-, etc.) the MW cut-off of ionized molecules could be considerably smaller [4, 5]. NF membrane separations already have significant industrial applications in the separation of dyes from salts [6, 7] and treatment of wastewater [6, 7, 8, 9]. However, although several possible applications exist in the food and pharmaceutical industries requiring the use of NF membranes with solvent streams, the fundamental behavior of these membranes with solvents is not well understood. Further, there is limited development into solvent resistant NF membranes in general. A fair amount of characterization has been done with KOCH membrane MPF series: MPF-44, MPF-50, and MPF-60 [10, 11, 12, 13]. Of these three membranes, the MPF-44 is considered to be hydrophilic with a slight negative charge while the MPF-50 and MPF-60 are hydrophobic membranes made specifically for the transport of hydrophobic solvents. Further, work has been performed with highly charged cationic and anionic membranes in the presence of ethanol [14, 15]. The study performed by this group has shown that methanol decreases the overall charge of the membrane. The goal of our work was to establish the effect of polar solvents on charged organic solutes with the permeation behavior of ionized membranes and use this knowledge to predict the flux and rejection behavior. With this in mind, we choose two strongly charged dyes, one negative and one positive, as well as p-amino benzoic acid (PABA) as model compounds for the rejection with negatively charged membranes. It was thought that the characterization with these three molecules would help understand both size and charge effects of rejection with solvent systems. Further, pure and alcohol-solvent systems were permeated through the charged membranes to help establish the effects of extremely hydrophilic solvents on membrane separation. Thus this paper will show: 1) Theory relating the membrane flux and ionization to measurable material parameters, 2) predicted and actual organic solute rejection as a function of pH in various solvents, and 3) the effect of solvents on the flux and rejection characteristics of charged nanofiltration membrane.

4.2 Background and theory

4.2.1 Aqueous systems

In order to help understand the results of NF membranes in non-aqueous systems, a fundamental understanding of aqueous systems is important. A standard rejection curve for organic molecules in aqueous solution has been established for various NF membranes [1]. The results of this study indicated that for non-charged organic molecules, the rejection increases as the size of the molecule increases. Using the standard equation for water flux in a pressure driven membrane is defined as:

$$J_w = A(\Delta P - \Delta \pi) \tag{1}$$

where A is the water permeability coefficient, ΔP is the applied pressure difference, and $\Delta\pi$ is the osmotic pressure difference. As can be seen, the flux will be expected to increase linearly with applied pressure. However, since a nanofiltration membrane has increased pore size over an RO membrane, the water permeability coefficient, A, will most likely be a function of both pore size due to convective flow and diffusive flow. Thus, the water permeability coefficient could be represented as a linear combination of these two terms as:

$$A = \frac{D_w C_w \overline{V_w}}{R_g T L} + \frac{\varepsilon R_p^2}{8 \eta \tau L} \tag{2}$$

where $\bar{D}_w$ is the diffusivity of the water, C_w is the concentration of water in the membrane, $\bar{V}_w$ is the partial molar volume of water in the membrane, R_g is the gas constant, T is the absolute temperature, ε is the membrane porosity, R_p is the pore radius, τ is the tortuosity, η is the solution viscosity, and L is the membrane thickness. With Equation 2, depending on the particular characteristics of the membrane in question, either the first (diffusive flow) or second (convective flow) term may dominate the separation. For the modeling of the solute flux, the convection, diffusion, and electrical (Donnan) repulsion must all be considered. This has been performed extensively in literature with the Nernst-Planck Equation successfully describing systems of electrolytes in water [3, 16, 17]. The Nernst-Planck Equation is defined as:

$$J_s = D_s \frac{dC_s}{dx} - \frac{z_i C_s D_s F}{R_g T} \frac{d\Psi}{dx} + J_w C_s \qquad (3)$$

where J_s is the solute flux, D_s is the solute diffusivity, C_s is the concentration of solute in the membrane, z_i is the charge of the solute, F is Faradays constant, and ψ is the Donnan potential of the membrane. The three terms in this equation represent flow due to diffusion, electrical repulsion, and convection, respectively. The understanding of the transport of each of these three terms may be important, especially with charged ions. For instance, with a negatively charged membrane, the rejection of NaCl, Na_2SO_4, and Na_3PO_4 increases, respectively. The main reason for this increase is the electrical repulsion increase with the -1, -2, and -3 co-ion charge. This phenomena has been well studied and is known as Donnan exclusion [18, 19, 20]. Donnan exclusion is very dependent on the charge of both the membrane and the solute. Thus, change in charge by either the solute or the membrane can affect both the water flux and the rejection.

When a membrane has a strong negative charge (negative in the entire pH operating range) then the rejection characteristics of low to moderate molecular weight compounds are based solely on the charge of the molecule being rejected. For a negatively charged organic compound, the pK_a of the organic will be important for the rejection behavior. For instance, below the pK_a, the rejection will be much lower than above the pK_a because of the reduction in charge. For this reason, rejection can be given as a function of pH as:

$$R = K_1(10^{-pK_a})/(10^{-pK_a} + 10^{-pH}) + K_2 \qquad (4)$$

where R is the rejection of the ionizable molecule, and K_1 and K_2 are constants determined by a membrane-solute rejection experiment at two different pH values. It is best if the two experiments include one point significantly below the pK_a and one point significantly above the pK_a. This equation is accurate for charged membranes at all pH values where the membrane functional group is ionized. However, the constants K_1 and K_2 must be adjusted for changes in membrane, solute, and solvent.

4.2.2 Non-aqueous systems

With non-aqueous systems, the interaction of both the solute and the solvent must be considered. With RO membranes, the interactions of solutes with the surface has been studied extensively [21, 22, 23]. The interactions of solutes have been shown to change the rate of solvent transport through the membrane.This is because the solute occupies many of the solvent transport sites, which take up the total number of sites available for water transport [21]. However, when dealing with pure solvents, the solvent-membrane interaction can be correlated by solubility parameters. Solubility parameters have been extensively used to establish polymer-solvent interactions [24, 25]. If a polymer and a solvent have similar solubility parameters, for instance, the polymer is likely to be soluble in the solvent. The solubility parameter is defined as the square root of the cohesive energy density, or energy to keep the fluid in the liquid state. It can be estimated by the following [26]:

$$\delta = \frac{\Delta E_i^{vap^{1/2}}}{V_i} \tag{5}$$

where ΔE_i^{vap} is the heat of vaporization and V_i is the partial molar volume. Further, as discussed by Hansen [27], the solubility parameter may be broken up into the contribution of the different forces associated as:

$$\delta^2 = \delta_h^2 + \delta_p^2 + \delta_d^2 \tag{6}$$

where δ_h, δ_p, and dd are the solubility parameters for hydrogen bonding forces, dipole-dipole forces, and dispersive forces, respectively. If the solubility parameters of a membrane are close to that of a solvent (without miscibility), the flux of that solvent through the membrane is expected to be high. Recalling Equation 2, for cases when convective flow is dominating, the flux would be expected to be linear with $1/\eta$. However, this is assuming that the solvent has no effect on the pore hydration. With a highly charged membrane, dehydration may lead to a decline in pore size making the simple viscosity relationship invalid.

The factors determining rejection and flux of charged NF membranes are occupancy of the solvent transport sites as well as the charge on the solute. It has been well established that solvents affect the charge of organic molecules in solvents such as methanol [28], ethanol [29, 30], and propanol [31]. This is because solvents suppress the ionization of most organic solutes and the membrane functional group ionization. A detailed theory of this phenomena has been established by Bates [32]. The analysis of this model as related to the context of this paper will be presented below.

The effect of solvent concentration on the overall charge can be represented by activity coefficients as compared to that of water. The definition of this activity coefficient is shown as:

$$\gamma_i = {}_m\gamma_i \langle {}_s\gamma_i \tag{7}$$

where ${}_m\gamma_i$ is the solvent medium effect and ${}_s\gamma_i$ is the concentration effect of the activity. The concentration effect ${}_s\gamma_i$, is 1 at very dilute concentration. It is a measure of the interionic and ion-molecule forces. This term can be best represented by the Debye Hückel equation as:

$$-\log_s \gamma_i = \frac{(1.82455 \times 10^6) z_i^2 \sqrt{I\rho}}{(D_e T)^{3/2}\left[1 + 50.2904 (D_e T)^{-1/2} a_3 \sqrt{I\rho}\right]} \tag{8}$$

where a_s is the ion size parameter, ρ is the density of the solvent, D_e is the dielectric constant, and I is the molar concentration of the solvent. For organic solvents and water, this equation works very well for the estimation of ${}_s\gamma_i$. However even more important than calculating the concentration effect is the solvent medium effect. In these cases, the activity coefficients would best be measured experimentally by using the free energy of the system [32].

After estimating the overall activity coefficient, this relationship can be used to find the solute and/or membrane activity in the presence of solvent media. The most important determination is finding the pK_a of the solute as a function of solvent concentration. The pK_a in solvent media is different than what is thought of in an aqueous media. At high solvent concentrations, the pH of the solvent media is the concentration of hydrogen ion if only water was in the system. For instance, 1 cm^3 of water at pH 7 added to 99 cm^3 of ethanol, still has a pH of 7. By the same account, the pKa is still the hydrogen ion concentration at 50 % ionization. Thus, using the medium effect of the activity coefficient, the change in pKa in a solvent media can be written as [31]:

$$\Delta pK_a = \log_m \gamma_{H^+} + \log_m \gamma_{A^-} - \log_m \gamma_{HA} \tag{9}$$

where the different medium activity coefficients refer to the dissociation of the molecule and ΔpK_a is the change in the pK_a as a result of the solvent in the system. With alcohols, the addition to water causes a pronounced increase in the pK_a The net result is, although Equation 4 could still be used for the prediction of behavior in the solvent media, a new pK_a must be considered.

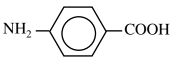
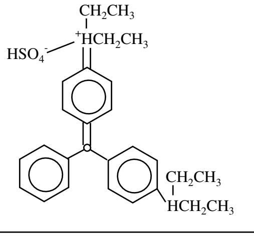
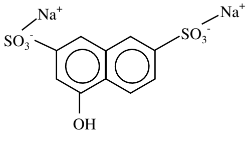
4.3 Experimental

Two different membranes were used for the nanofiltration experiments in this study. These membranes include Desal 5 Membrane and Desal HL Membrane (Osmonics Inc.). The Desal 5 membrane is a slightly negatively charged nanofiltration membrane cast on a polysulfone backing. The Desal HL Membrane is a highly negatively charged nanofiltration membrane cast on a polysulfone backing. Both membranes are extremely hydrophilic.

The nanofiltration experimentation was done using a stirred cell batch filtration unit with an effective area of 122 cm^2. The system was a well-mixed batch system (2 L volume) with nitrogen gas controlling the overall pressure. Although this apparatus could control the concentration polarization by simply controlling the rate of mixing, that was not one of the variables to be studied in this research and so mixing was always kept at the maximum attainable assuring high Re numbers. A standard characterization run consisted of pure water flux, followed by 2,000 mg/L Na_2SO_4 flux and rejection, followed again by a pure water flux. All three of these experiments were performed at 6.9 bar. An example of an expected result, with the Desal 5 membrane, is 13–14 x 10^{-4} cm^3/cm^2s pure water flux (6.9 bar), 96 % rejection with Na_2SO_4 at 2,000 mg/L. The behavior of the Desal HL membrane was similar in terms of rejection (95 %) and membrane pure water flux of 16–18 x 10^{-4} cm^3/cm^2s at 6.9 bar. For most membrane trials, this characterization was made periodically to classify membrane performance changes.

Three model organics were used in nanofiltration separations: brilliant green (BG), 1-Naphthol-3,6-Disulfonic Acid (NDSA), and p-amino benzoic acid (PABA). The permeation of these organics took place by mixing 1-2 L of 10–200 mg/L organic at pH 2–9 in water and placing it in the batch cell described above. Two of these organics, BG and NDSA, have been used by membrane manufacturers for characterization. The standard physical properties of these three organics are shown in Tab. 4.1. In certain situations, various concentrations of salts (NaCl) ranging from 1–5 % were added with the organics.

Tab. 4.1: Characteristics of organic molecules used in this research.

Molecule	**Structure**	**MW**	**UV Absobance**	**Linear Calibration (mg/L)**	**Accuracy (%)**
p-amino benzoic acid		135	264	2–10	1.6
brilliant green		483	624	1–10	3.2
1-Naphthol-3,6-Disulfonic acid, Sodium salt		348	300	1–15	4.0

Three analytical techniques were used in conjunction with the nanofiltration experiments. These techniques were UV absorption, conductivity, and total carbon (TC). Total carbon (TC) was measured on a Beckman Tocamaster Total Organic Carbon Computational System. Samples (30 mL) were injected to the instrument operating at an air flow rate of 2.5 cm^3/min, carrier gas temperature of 55°C, and oven temperature of 950°C (the Tocamaster has a catalyst to insure complete combustion). The instrument has an Infra-Red (IR) detector which senses the concentration of CO_2 in the combustion product. Calibration standards (potassium hydrogen phthalate) were used to calibrate unknown samples in the ranges of 50–250 mg/L TC. Different linear calibration ranges can be used provided that a different injection volume and a different calibration curve is used to insure linearity. The TC analyzer had an experimentally determined error of <3 %.

UV absorption was performed with a HP-8452A diode array spectrophotometer. The spectrophotometer works on the principle of shining light through a liquid sample and measuring the amount adsorbed. The linear calibration range for each of the compounds is also given in Table 4.1. As shown, the experimentally determined accuracy for three compounds ranges from 1.6–4 %. Conductivity was measured using an Amber Sciences Inc. Conductivity Meter. Conductivity (single components only) were measured in mho/cm against a standard calibration of sodium sulfate (linear from 40 to 2000 mg/L). Since the conductivity measurements were used only when high concentration salts were used, interferences were not shown to be significant for the concentration of organics used.

4.4 Results and discussion

4.4.1 PABA separation characteristics in aqueous systems

Charged NF membranes are used for the separation of many organic molecules. Since a significant amount of work had been performed on organic adsorption by RO membranes, NF membranes were characterized with a model organic compound to establish the role of adsorption and pH on membrane performance. The model compound chosen for the study was p-amino benzoic acid (PABA). PABA is an interesting molecule from a research standpoint because it has a positive charge at low pH (amine pK_a=4.65) and a negative charge at higher pH's (carboxyl pK_a=4.80). Keeping this in mind, Fig. 4.1 shows the rejection of PABA vs. pH for water, methanol, and ethanol systems. As shown, even at pH 3 ($\approx$100 % positively charged in water), the rejection of PABA in water was around 25 %. Also shown in Fig. 4.1, a model for the rejection based on ionization (Equation 4) is plotted. The model utilized only two data points: one around pH 3 and one above pH 7, which yielded constants of K_1 and K_2 (Equation 4) of 64.3 and 26.0, respectively. As shown, the model predicted NF rejection in water reasonably well. The r^2 of the model with the overall rejection is 0.98. Although there is slight negative deviation from the model to the actual data, the overall fit is reasonably good.

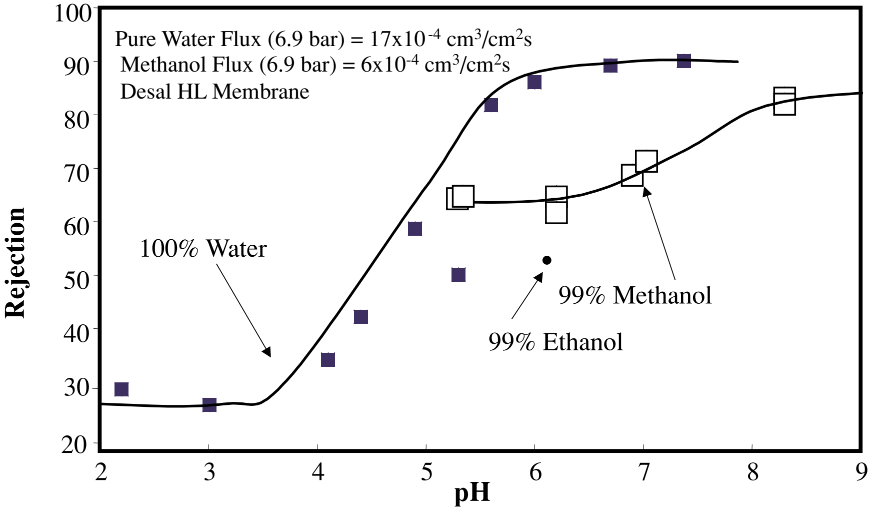


Fig. 4.1: Membrane flux and rejection of 100 mg/L PABA in an water, methanol, and ethanol systems.

Further, predictions can also be made for PABA rejection in methanol as a function of pH. To do this, the pKa of PABA in a 99 % methanol solution must be calculated. The data used was found in the work by Sarmini and Kenndler [28, 29, 31] shown in Fig. 4.2 for benzoic acid. It is interesting to note from this figure that methanol causes a different shift in the pKa than ethanol or propanol which may be caused by a difference in these three alcohols to support ionization [33, 34]. Using the data from Fig. 4.2, we assumed that PABA and benzoic acid have similar change in pKa of the carboxyl group. Thus, by extrapolating the data to 99 % methanol we have found a predicted pK_a of 7.2. Using this pKa and Equation 4, the prediction of the rejection (in methanol) using pH 5.2 and pH 8.2 can also be seen in Fig. 4.1. As shown, the methanol (21.1 and 62.8 for K_1 and K_2, respectively) goes through a transition predicted by that of the pK_a. However, the rejection at high pH and low pH are drastically different than that observed in water. This change can be examined by looking at the different mechanisms of transport. Below the pKa, the rejection of PABA is more than that of water. It has been found that the transport through NF membrane pores is often a function of the sorption of the solvent in the membrane [35]. Thus, since the negatively charged NF membrane is expected to have a lower sorption of methanol than water thus may enhance the rejection. The increased rejection at high pH is due to increased ionization of PABA. Finally, it is important to have an understanding of how the effects of solvent concentration in water on the rejection of PABA at completely ionized conditions. It would be expected that as solvent % increases, the rejection would decrease (above the pKa) since the overall charge is expected to be less than in organic solvent. Figure 4.3 indeed shows that PABA rejection decreases with ethanol concentration.

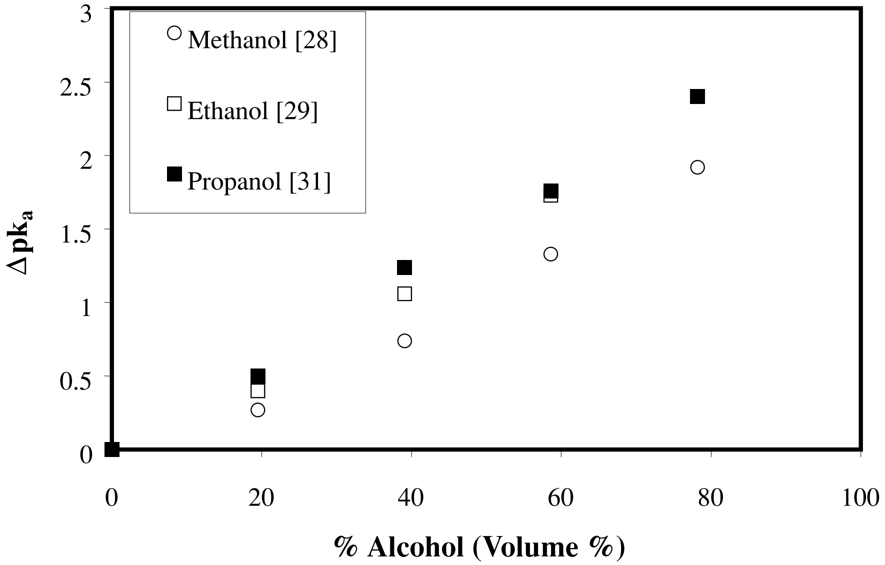


Fig. 4.2: The effect of solvents (alcohols) on the pKa of dilute benzoic acid in aqueous solutions.

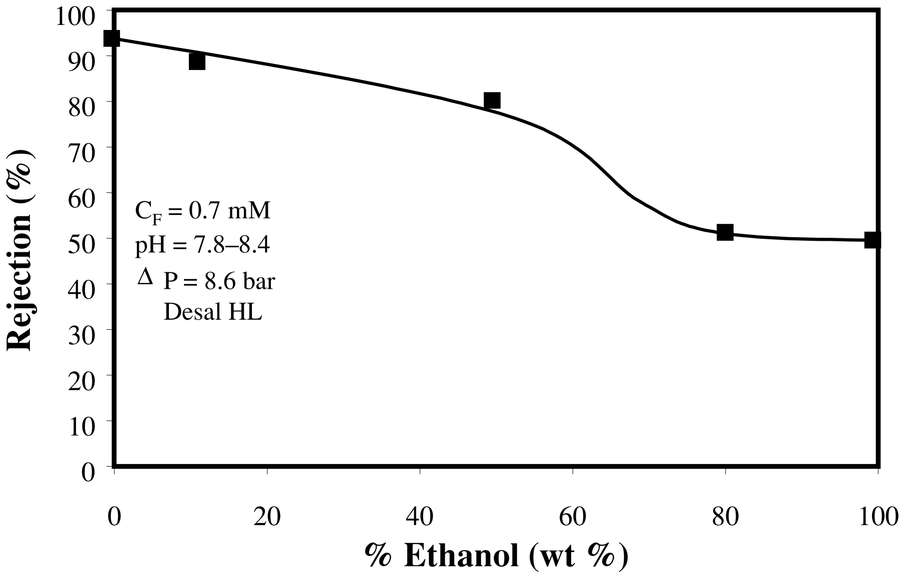


Fig. 4.3: The Relationship between p-Amino Benzoic Acid (PABA) Rejection and Ethanol Concentration

4.4.2 Rejection and flux behavior of positively and negatively charged dyes

The effect of solute charge on NF rejection and flux was also studied with Desal 5 membrane for the separation of BG and NDSA dye. As opposed to PABA, these dyes have strong charges and thus should be ionized at all pH values in streams containing a significant amount of water. However, the pH of all of these experiments was kept between 6-7 to assure this assumption correct. As can be seen in Fig. 4.4 for both dyes, the presence of ethanol in the feed affects the flux and the rejection characteristics. For NDSA, the rejection is observed to decrease from 92.8 % to 84.9 % and flux (in the presence of 5 % NaCl) through the membrane drops from 6.7×10^{-4} cm^3/cm^2s to 3.0×10^{-4} cm^3/cm^2s as the ethanol concentration in the feed is increased from 0 to 33 wt % (keeping all other variables constant). For BG dye, the rejection is observed to decrease from 97.0 to 84.7 % and the flux varies from 8.0×10^{-4} cm^3/cm^2s to 4.6×10^{-4} cm^3/cm^2s over the same ethanol concentration range. Thus it can be concluded that the presence of an organic solvent does affect the NF membrane permeation characteristics for the slightly negatively charged membrane, also. As discussed above, a decrease in the charge potential of the membranes and solutes lead to this decline in rejection.

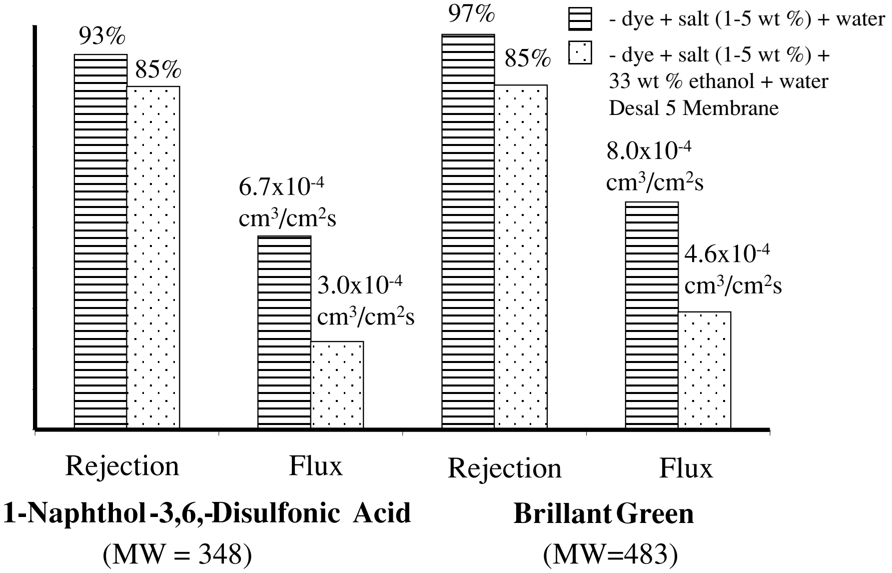


Fig. 4.4: Flux and rejection of BG in water and water-ethanol systems.

Finally, the NF flux was examined at high NaCl concentrations since these situations arise in many pharmaceutical operations [36]. Although a negatively charged NF membrane could have high rejections of salt at low concentration due to charge repulsion (Equation 3), at high concentration of salts, the charge effects would become masked and it would be expected that the rejection of the salt decreases significantly. For these reasons, NF experiments were performed with BG dye-salt-water mixtures using the Desal 5 membrane to study the flux and rejection characteristics of the membrane in presence of the salt. Figure 4.5 shows the effect of the salt on the flux and the dye rejection of the membrane. The dye concentration was kept constant at 15 mg/L whereas the salt concentration was varied from 0 to 5 wt %. The pure water flux through the membrane is 14×10^{-4} cm^3/cm^{2}s at a 6.9 bar operating pressure. The relative flux (actual flux/pure water flux) is observed to decrease from 0.78 to 0.46 (flux over distilled water flux) as the salt concentration is increased from 0 to 5 wt%. This result is expected since as the salt concentration is increased, the partial rejection of the salt ions decreases. However, the net osmotic pressure difference (Δp) increases and hence the flux decreases. The dye rejection is constant at 98 % over the entire range of salt concentration. Thus it can be concluded that the dye rejection is not affected in the presence of the salt. Finally, it is interesting to note that because of the strong positive charge, BG, at very low concentrations, causes a significant decline in the flux. Presumably, the flux decline is much more than that seen by PABA because of the size and hydrophobicity of the molecule.

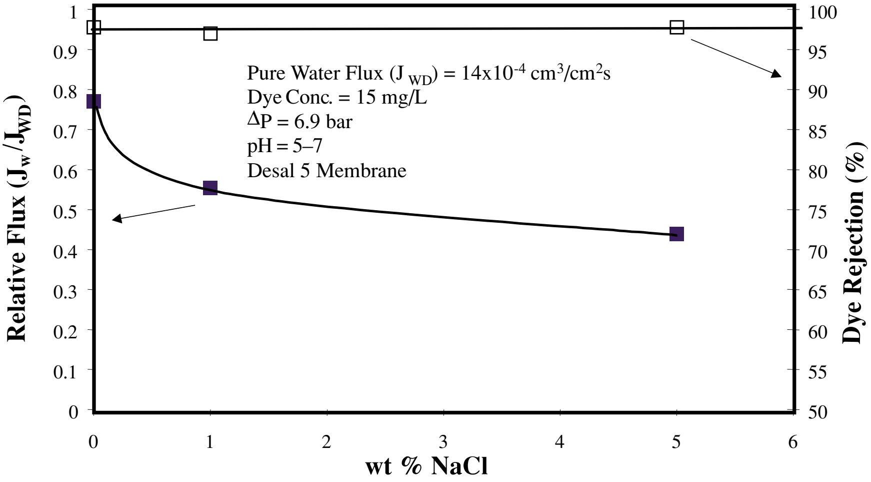


Fig. 4.5: The effect of NaCl concentration on flux and rejection of brilliant green dye.

4.4.3 Pure solvent and water-solvent flux

As has been shown, solvents have a profound impact on the rejection of organic solvents with charged NF membranes. As well as the prediction of rejection, it is also important to study the flux of pure organic solvent and aqueous/organic solvent systems, especially without the presence of solute. To establish the affects of solvents on membrane performance, pure solvent studies were first conducted with a negatively charged NF membrane (Desal HL). Since this membrane is highly hydrophilic, it was thought the flux would have a relationship with either the dipole-dipole or the hydrogen bonding solubility parameter. As shown in Fig. 4.6, as the solvent becomes more hydrophobic, the flux through the membrane becomes significantly lower and correlates well with the dipole-dipole solubility parameter. In fact, hexane flux is over 50 times lower than water flux. Further, it is possible that the solvent is even causing the NF pores to shrink by dehydrating the tightly bound water from the membrane and that this is part of the reason for the flux decline. This is consistent with the evidence found for the NF rejection. As also can be seen with the data from Fig. 4.6, below a certain polar solubility parameter (7 MPa$^{1/2}$) there is no further decrease in flux. This is because with solvents like IPA and hexane the membrane reaches a maximum dehydration of solvent from the charge sites. Finally, it is interesting to note that in the work by Sirkar et. al [37] with negatively charged MPF-44, it can be seen that the ratio of methanol/water flux is approximately 0.5. Considering the ratio found in our work for the Desal HL membrane of 0.35±0.04, it can be concluded that these charged membranes have similar behavior in the presence of alcohols although the Desal HL membrane may be slightly more hydrophilic.

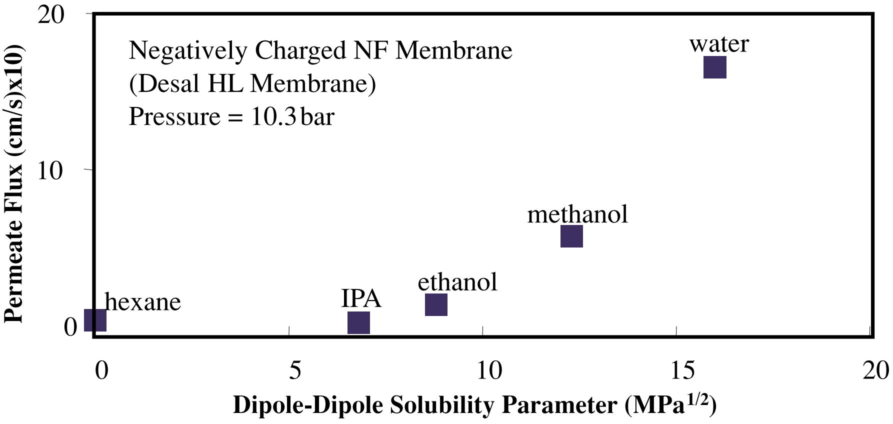


Fig. 4.6: Correlation of dipole-dipole solubility parameter with membrane flux.

As would be predicted by Equation 2, for cases when the membrane dehydration does not occur, the flux would be expected to have a linear relationship with inverse viscosity if convective flow is the dominating mode of transport. It was thought at low alcohol concentrations, even for the highly charged Desal HL nanofiltration membrane, this would be the case. For these reasons, experiments were conducted using highly charged NF membranes with aqueous mixtures of methanol and ethanol. The results of this study can be seen in Fig. 4.7. Given this drastic change in flux going from 0–10 wt % alcohol, it was desired to see if this effect is viscosity dependent. It has been well

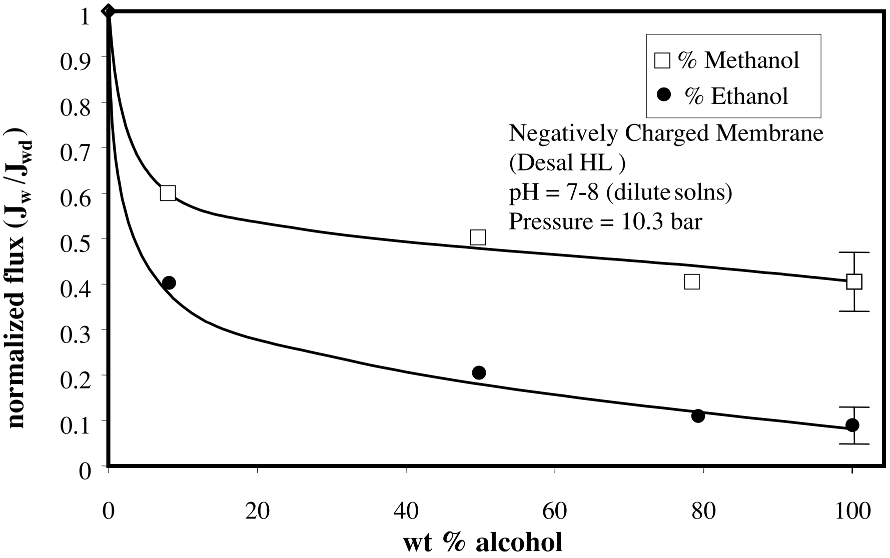


Fig. 4.7: Permeate flux as a function of alcohol concentration.

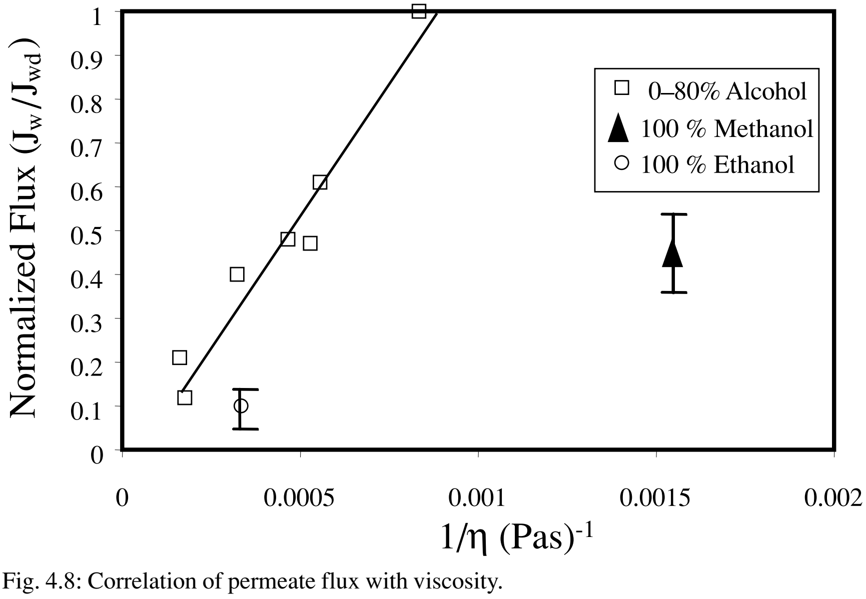


Fig. 4.8: Correlation of permeate flux with viscosity.

documented that both ethanol and methanol go through a large positive deviation in viscosity at low wt % alcohol. Thus, Fig. 4.8 shows the plot 0–80 and 100 wt % alcohol. As shown, the correlation of $1/\eta$ is quite valid in the low concentration range ($r^2 > 0.94$)

but quite poor if the high wt % alcohol is included ($r^2 < 0.25$). This demonstrates that the viscosity relationship works well for describing flux behavior until pore dehydration becomes significant. Further, the fact that the relationship with inverse viscosity fits well is proof that for this membrane convection is the dominating mode of transport. Finally, it is interesting that attempting to correlate the pure solvent flux (Fig. 4.6) with viscosity yields no significant trend ($r^2 < 0.05$). This is consistent with the conclusions of Machado et. al [11] who also found that a convection model only cannot be used to explain pure solvent behavior in NF membranes.

4.5 Conclusions

The purpose of these studies was to show the separation characteristics of charged NF membranes in water and solvent-water media and relate these properties to measurable parameters such as viscosity and solubility parameters. It has been shown that a negatively charged organic rejection increased with pH when separated with negatively charged NF membranes. This increase in rejection is mainly due to the pKa transition of the organic molecule. For this reason, organics, which shift the pKa, are shown to have rejection increases at much high values of pH. As well as the rejection characteristics of organics, the flux of NF membranes in the presence of both solvents and salts were established. With highly hydrophilic NF membranes, increasing hydrophobicity of solvents (measured with solubility parameters) were shown to decrease the flux through the membrane due mainly to membrane solubility and a decrease in pore size in the membrane polymer morphology. However, aqueous systems with low alcohol concentration followed a trend dictated by the solvent-water mixture viscosity.

Acknowledgements

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5 Industrial Membrane Reactors

M. F. Kemmere and J. T. F. Keurentjes

5.1 Introduction

Over the past decades, membrane processes have found broad application for a wide range of separations. The first large-scale applications of membrane technology can be found in brackish water desalination using reverse osmosis and hemodialysis. Based on the different driving forces applied, the range of separations can be divided into various filtration processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), gas and vapour separation, pervaporation and electromembrane processes (including electrodialysis, membrane electrolysis and bipolar membrane processes). Additionally, based on preferential wetting properties, porous membranes have been used as a support for liquid membranes and for various contactor applications (including membrane-based solvent extraction and gas absorption). These processes usually focus on a desired separation of a gas or liquid mixture.

When it comes to combination with a reaction or conversion, membranes have mainly found application in a sequential mode, i.e. reaction followed by separation. In this chapter, we will focus on the integration of conversion and separation in so-called membrane reactors. As the separation function of the membrane can be used in various modes of operation, this leads to a broad variety of process options. In the past few years, several review papers have emerged, usually covering parts of this huge research field [1–5]. The general advantages of membrane reactors as compared to sequential reaction-separation systems are:

- Increased reaction rates
- Reduced by-product formation
- Lower energy requirement
- Possibility of heat integration

These advantages potentially lead to compact process equipment that can be operated with a high degree of flexibility. Because of the reduced by-product formation and the more efficient use of energy, the development of membrane reactors clearly fits into the scope of developing sustainable processes for the future.

First applications of membrane reactors can be found in the field of bioprocess engineering using whole cells in fermentations or enzymatic bioconversions [6, 7]. Most of these processes use polymeric membranes, as temperatures seldomly exceed 60 °C. The development of inorganic membrane materials (zeolites, ceramics and metals) has broadened the application potential of membrane reactors towards the (petro)chemical industry [8]. Many of these materials can be applied at elevated temperatures (up to 1000 °C), allowing their application in catalytic processes.

The basic functions of the membrane in membrane reactors can be divided into (Fig. 5.1):

- Selective and non-selective addition of reactants
- Selective and non-selective removal of reaction products
- Retention of the catalyst

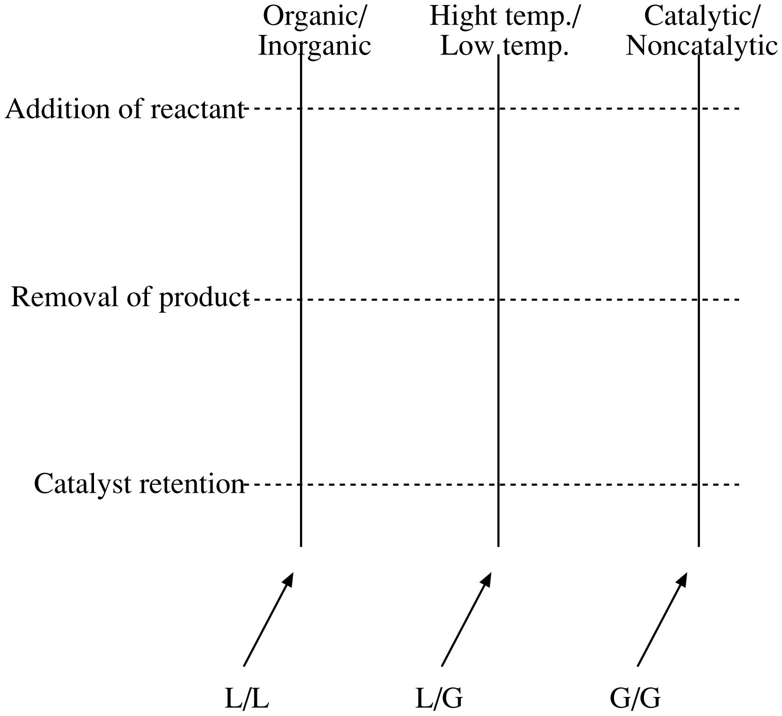

Fig. 5.1: Schematic overview of the basic functions membranes can have in membrane reactors.

As the membrane acts as a separating medium between two flow compartments, these basic functions can be applied to liquid/liquid, gas/liquid and gas/gas systems, respectively. The physical shape of the membrane strongly depends on the membrane material used. For polymeric systems, these can be flat sheets in a plate-and-frame configuration, spiral wound modules, and tubular membranes and hollow fibers in a shell-and-tube configuration, respectively [9]. The first two systems will not easily allow for independent flow of both compartments, as the permeate chamber can not be flushed.

On the other hand, spiral wound modules allow for a large surface area per volume (typically 1000 m^2/m^3). Even more area per volume can be obtained in hollow fiber units, for which a typical value is around 10,000 m^2/m^3. Most polymeric membranes can not be applied at temperatures above 100–150 °C, which implies that for these conditions inorganic membranes have to be used. These can be produced in several shapes: flat plates, tubes, multi-hole elements and hollow fibers. Although the hollow fiber systems are still in an early stage of development [10–13] they represent a promising group of materials, especially due to the high surface area per volume that can be obtained.

With respect to catalytic membrane reactors, processes can be divided in homogeneously and heterogeneously catalyzed reactions, see Fig. 5.2. In homogeneously catalyzed processes, the membrane modules can be used in loop reactors. For heterogeneously catalyzed reactions several configurations are possible:

- The membrane units and fixed bed catalysts can be applied in series
- The fixed bed catalysts can be integrated in the membrane module
- The membrane itself can have the desired catalytic activity

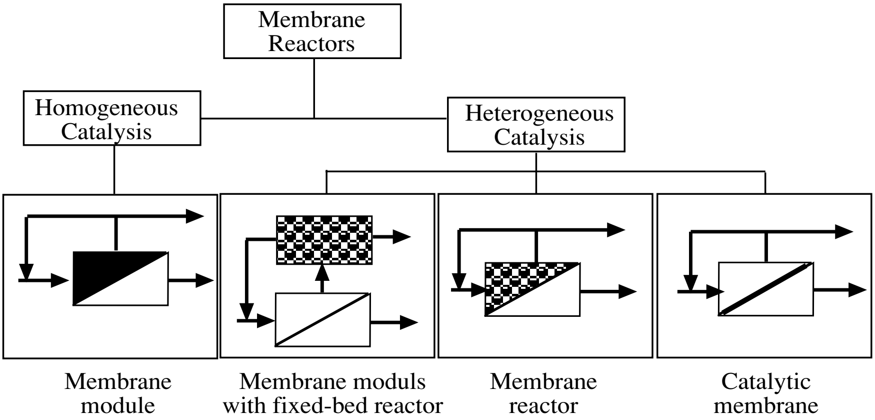

Fig. 5.2: Classification of catalytic membrane reactors [14].

In the following sections, we will discuss the developments in the field of membrane reactors. Emphasis will be on the application potential of the various options on a large scale. The set-up will be along the lines of the three basic functions the membrane can have in these systems. Finally, some developments that have led to applications on an industrial scale, or which are relatively close to this, will be described in more detail.

5.2 Membrane functions in reactors

The most generic distinction in the wide variety of membrane reactors can be made according to the possible functional roles of the membrane in the reactor, being controlled addition of reactants, separation of products from the reaction mixture and retention of the catalyst. Additionally, membrane processes can be divided based on the physical state of the retentate and permeate, respectively:

- liquid/liquid systems such as microfiltration, ultrafiltration,nanofiltration, reverse osmosis, liquid/liquid contactors and dialysis
- liquid/gas systems like pervaporation or gas/liquid contactors
- gas/gas systems such as gas permeation.

Based on a major division by membrane function in the reactor, a number of examples of membrane reactors are given below, illustrating the importance of the use of membranes for combining reaction and separation. Obviously, the list of membrane-based processes described here will not be exhaustive, although the following paragraphs will give an overview of the applications of membranes for chemical reactions.

5.2.1 Controlled introduction of reactants

The major advantage of using membranes for the addition of reactants comprises the independent control of the concentration levels of each reactant in the reaction zone. One reactant can be fed along the length of a reactor, as schematically shown in Fig. 5.3. This is commonly done in a tube and shell configuration. An additional advantage is the possibility to apply a permselective membrane for purification of a reactant from a mixed stream before addition into the reaction zone, e.g. utilising pure O_2 from an air stream. Also, the membrane can be used for the coupling of two reactions by physically separating the two reaction media and introducing the product of one reaction as a reactant for the second reaction.

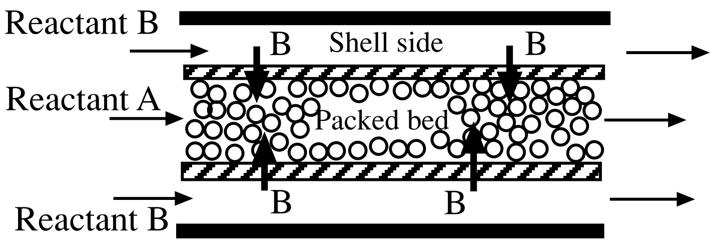

Figure 5.3: Schematic representation of a membrane reactor for controlled reactant feed [1].

Gas-phase reactions

For gas phase reactions, the controlled addition of reactants A and B can effectively be applied to systems with two competing reactions, e.g. partial oxidation of hydrocarbons:

$$A + \alpha B \xrightarrow{k_1} P \tag{1}$$

$$A + \beta B \xrightarrow{k_2} S \tag{2}$$

In this reaction scheme, P is the desired product and S is the undesired by-product. In the case the reaction rates are proportional to the partial pressure of reactant B ($r_1 = k_1 p_B^{n1}$ and $r_2 = k_2 p_B^{n2}$, respectively) the kinetics are favourable if $n1<n2$. Also, a lower pB will slow reaction 2 more than reaction 1, inducing an increased selectivity for the desired product P. For this purpose, mainly porous membranes are used. To control the uniformity of the distribution of B, the membrane should have sufficient resistance to equalise the pressure on the reactant side, i.e. a constant transmembrane pressure drop along the tube [15,16]. Another problem to tackle in this type of systems is back diffusion of reactant A and product(s) P and S. Here also, an increased pressure drop across the membrane will be advantageous, although it also decreases the permeation rate of B, which potentially leads to problems balancing the feed rate to the reaction rate 1.

In addition to the use of porous membranes, also dense membranes can be applied for controlled addition of reactants. In this respect, focus has mainly been on hydrogen and oxygen supply. For hydrogenation reactions, Pd-based membranes have been used [17, 18], resulting in improved yields. Nevertheless, this can not be attributed to the kinetics considerations given above, but is due to a better availability of H^+ at the membrane surface. Most of the work on dense membranes for controlled addition of reactants, however, has been done for oxygen supply. Despite the high temperatures required (> 700 °C), currently the main focus is on the application of solid oxides, with much emphasis on the use of various perovskites [19–23]. Controlled supply of oxygen has mainly been studied for the oxidative coupling of methane. Yields in excess of 50 % have been predicted theoretically, however, the experimental results have not exceeded 25–30 %, similar to fixed bed results. Both dense [19–23] and porous membranes [16, 24–26] have been used, both leading to similar results.

In addition to oxidative coupling of methane, several oxidative dehydrogenations have been investigated, including the conversion of ethane to ethene [15, 27, 28], propane to propene [29] and butane to butene [30]. In these systems, controlling the hydrocarbon to oxygen ratio was found to be crucial for selectivity (with respect to by-products like CO_2, CO, etc.). At low and moderate ratios, the ethene yield in the membrane reactor exceeds that in a cofeed plug flow reactor operated under the same conditions by a factor of 3. In the membrane reactor the reactant feed ratio near the inlet of the reactor is relatively high, resulting in a high selectivity. Continuous addition of oxygen along the tube ensures high conversion as well.

Non-permselective membranes can also be used to provide a location for a reaction zone. One reactant is fed on the tube side of the membrane, and the other reactant is fed on the shell side. The partial pressure gradients have to be chosen such that the two reactants permeate towards each other inside the membrane, where they can react. Usually, the membrane itself contains a suitable catalyst. In this type of membrane reactor, reactions are performed at a strict stoichiometric ratio. For fast reactions, this results in a reaction plane, whereas for slower reactions a reaction zone will be formed. This is shown schematically in Fig. 5.4. Balancing reaction rate and permeability can result in a reaction zone entirely located inside the membrane. When breakthrough of reactants can be avoided, and the product diffuses out on one side only, this can simplify the further separations required.

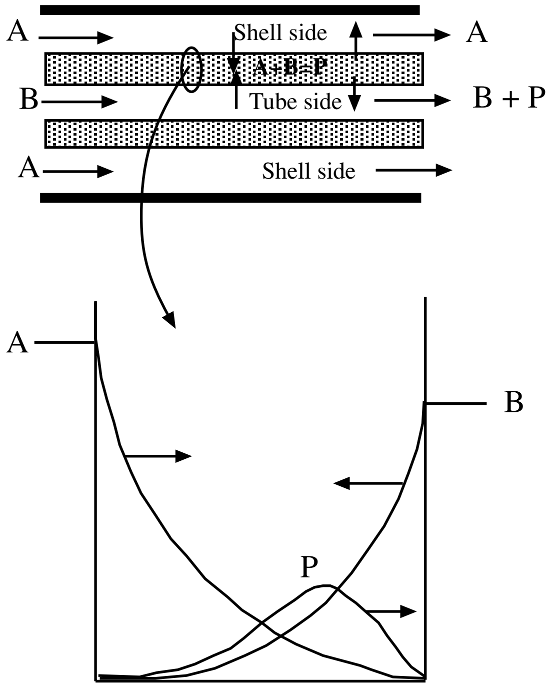

Fig. 5.4: Catalytic non-permselective membrane reactor with separated feed, showing transmembrane concentration profiles of the different species involved and the direction of permeation [1].

An example of this set-up is the dehydrogenation of methanol and butane using microporous g-alumina and Ag-modified g-alumina membranes as the catalyst [31–34]. The methanol and oxygen are fed on different sides of the membrane, thus minimizing undesired gas-phase reactions. Additionally, the catalytic activity of the membranes appeared to be 10 times higher than the activity of the same catalyst when packed. This is attributed to the effective regeneration of the catalyst. Since all oxygen passes through the catalyst layer, this allows for effective burning of the carbon deposit. A similar system was used for the reduction of nitric oxide with ammonia [34–37]. The ability of the membrane to act as a barrier between reactants has also been shown to be effective for the Claus reaction (Fig. 5.5) [38, 39]. In general, using the membrane as the reaction zone is of particular interest for fast, exothermic heterogeneously catalysed reactions, since runaway is prevented due to mass transport being the rate-limiting step [40].

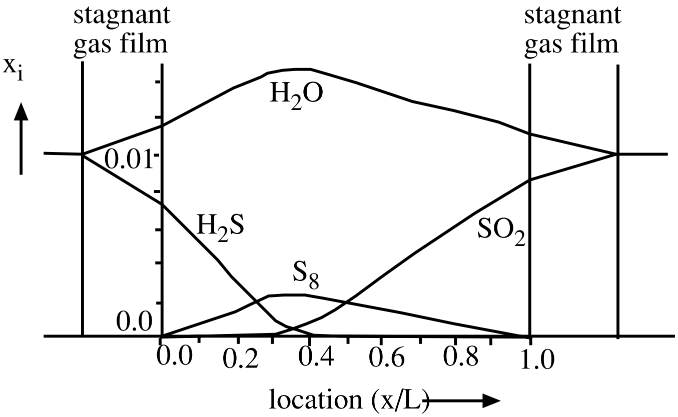

Figure 5.5: Molar fraction profiles at 200 ºC in absence of a pressure difference over the (non-permselective) membrane used for the Claus reaction [38, 39].

Liquid-phase reactions

The main application of membrane reactors for liquid-liquid systems is based on intimate phase contacting, without the formation of an emulsion. This avoids troublesome phase-splitting afterwards. Microporous membranes have proven to be particularly useful for this type of applications, since the two immiscible liquids can be kept on two sides of the membrane with their interface immobilized at the membrane surface [41–43]. The general advantages of these systems are: no dispersion is formed, thus avoiding coalescence; no density difference required between the two phases; large and known interfacial area (typically 10,000 m^2/m^3); no loading and flooding, thus allowing for widely different phase flow ratios. The application of membrane contactors for reactive systems has been explored for three types of systems: fermentor-extractor, enzymatic reactions (enzymatic hydrolysis/esterification and enzymatic resolution of isomers) and phase transfer catalysis (PTC).

In the group of Sirkar, the application of microporous hollow fibers in the fermentative production of ethanol, acetone-butanol-ethanol (ABE) etc. has been explored. In these systems, the role of the membrane is twofold. Firstly, oxygen or nitrogen is supplied and the reaction products CO_2 and H_2 are removed. Secondly, an organic solvent is passed through the fibers, extracting the products (ethanol, ABE) [44–47]. This reduces product inhibition and can therefore lead to considerable increased volumetric fermentor productivity.

When lipases are used for enzymatic conversions, the enzyme is mainly active at a phase boundary, which can effectively be provided by a membrane. Additionally, for conversions requiring two phases (e.g. fat splitting [48–50] and esterifications [51]), the membrane also keeps the two liquid phases (an oil and an aqueous phase, respectively) separated. This is schematically depicted in Fig. 5.6. The equilibrium reactions involved are

Triglycerides + water <-> diglyceride + fatty acid (3)

Diglyceride + water <-> monoglyceride + fatty acid (4)

Monoglyceride + water <-> glycerol + fatty acid (5)

The use of both hydrophilic [49, 51] and hydrophobic [48, 50] membranes have proven to be efficient in binding the enzyme. The main advantage of this system as compared to emulsion systems lies in the ease of the downstream processing, as no enzyme-stabilized emulsion has to be broken.

In addition to the enzymatic fat splitting and esterifications, a multiphase extractive enzyme membrane reactor is being used for the industrial production of a diltiazem chiral intermediate. This process will be described in more detail in section 3.5.

Phase transfer catalysis has been investigated for the model displacement reaction of bromooctane with iodide. The first is dissolved in an organic solvent (chlorobenzene) and the latter in an aqueous phase. The phase transfer catalyst used was the tetrabutylammonium ion, dissolved in the organic phase [52]. Using a hydrophobic membrane contactor device, conventional coalescence problems were avoided. Additionally, as a result of the interfacial area being known, operation of the reactor can be performed with greater flexibility.

Gas-liquid reactions

Reactions requiring both a gaseous and a liquid reactant are usually performed in trickle bed reactors in which the gas and liquid are pumped counter or cocurrently through a bed of catalyst particles [53, 54]. Many of these systems encounter mass-transfer limitations as a result of intraparticle mass-transfer resistance, liquid-film resistance, liquid maldistribution and channelling. To overcome these problems, membrane reactors have been used for chemical reactions as well as biological conversions.

Gas-liquid reactions investigated are the hydrogenation of α-methylstyrene to cumene using a porous γ-alumina membrane impregnated with a Pd catalyst [55] and the hydrogenation of nitrobenzene to aniline in a Pt-impregnated porous γ-alumina membrane [56]. From both studies is was concluded that the membrane reactors can be per-

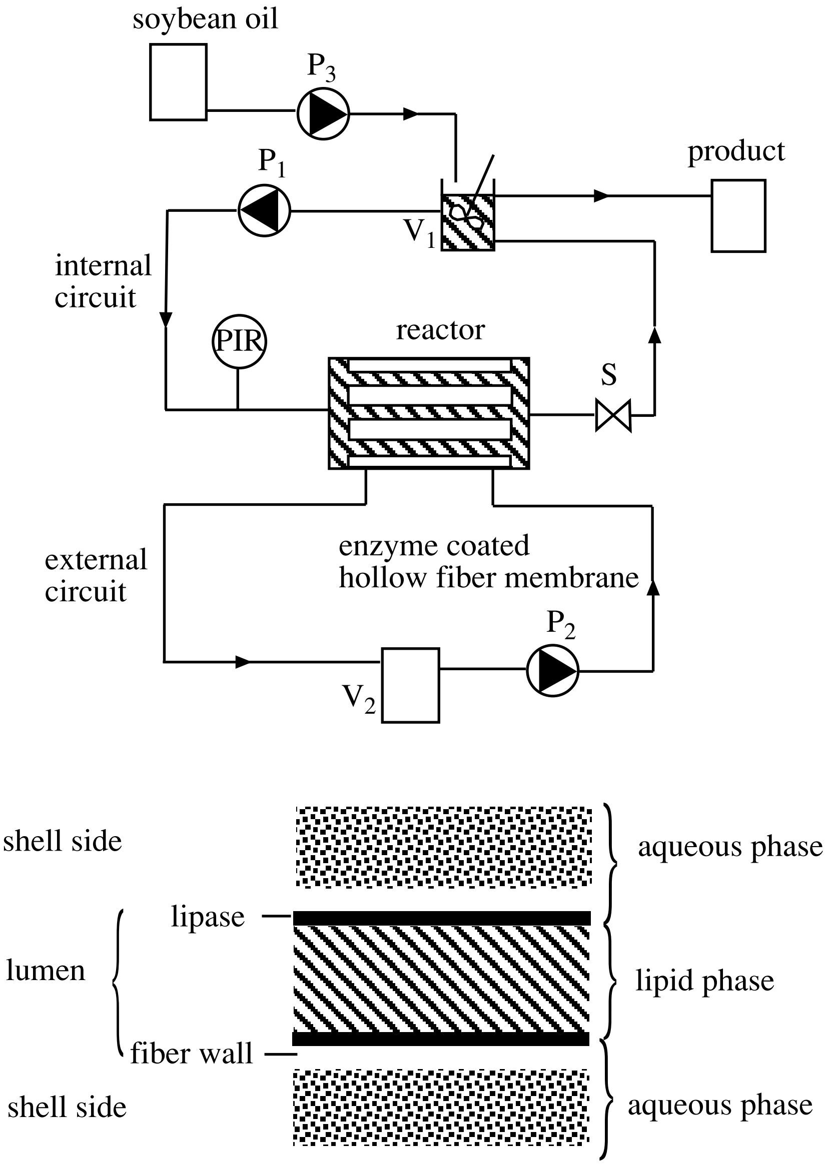

Fig. 5.6: Experimental setup (top) and schematic representation of a cross section through a hollow fibre (bottom) for the enzymatic conversion of triglycerides into fatty acids [49]. For this purpose a hydrophilic membrane is used, coated with the enzyme (lipase) on the lipid side.

formed without any operational problems and that reaction rates increased significantly (up to factor of 20) as a result of easy access of the gas to the catalytically active sites.

Biotreatment of large air streams in membrane contactors has been evaluated widely (Tab. 5.1 [57]). The removal of organic compounds (e.g. propene, dichloromethane, etc.) and inorganic substances (SO_2, NO_x etc.) has proven to be highly efficient in membrane contactors. The gas stream to be treated is led on one side of the membrane, whereas an appropriate aqueous solution containing a one single or a mixture of bacteria is circulated on the other side. This allows for an easy adjustment of conditions (pH and nutrients). The bacteria used can either grow as a film onto the membrane surface or can be homogeneously dispersed in the liquid. This approach has led to large-scale operations, e.g. for the treatment of traffic tunnel vent streams.

Tab. 5.1: Membrane bioreactors for biological waste gas treatment in historical order [57].

Ref.	Compound removed from air	Conc. [ppm]	Type of membrane	Nutrient supply in liquid	Bio-film	Inoculant
58	Xylenes	30–140	Silicone,tubes	Minerals	Yes	Sludge
58	n-Butanol	40–180	Silicone,tubes	Minerals	Yes	Sludge
58	Dichlormethane	60–220	Silicone,tubes	Minerals	No	Sludge
59	Toluene	20	HM[a],sheet	Minerals	NA[b]	Pseudomonas,GJ40
59	Dichlormethane	47	HM, sheet	Minerals	NA	Strain DM21
60	Toluene	56	HM,sheet	Minerals	Yes	Pseudomonas GJ40
60	Diclormethane	69	HM,sheet	Minerals	YES[c]	Strain DM21
61	n-hexane	32	Silicone, tubes[d]	Minerals	?	?
61	Toluene	32	Silicone,tubes	Minerals	?	?
62	NO	5	H,sheet	Alcohols, Minerals	Yes	Methylobacter
63	Mixture	'low'	HM,sheet	Minerals	Yes	Various strains
64	Dichloretane	150	Silicone	Minerals[e]	Yes	Xanrhobacter GJ10
65	Propene	250–300	spiral wound HM,sheet	Minerals	Yes	Xanthobacter Py2
66	Trichloroethene	20	Polysulfone Fibres	Acetate, Minerals[f]	Yes	Sludge
60	Propoene	330–2700	HM,fibres	Minerals	Yes	Xanthobacter Py2

a: H, hydrophobic material; M, microporous material
b: Experiments lasted less than 1 day
c: Severe sloughing observed after 4 days
d: Reactor in a combination of a membrane bioreactor and a buble-column and was designed for simultaneous degradation of both hydrophilic and hydrophobic contaminants from the gas phase.
e: Gas phase did not contain oxygen
f: Liquid phase was kept anaerobic

5.2.2 Separation of products

In general, a reversible reaction such as (6) is often limited in conversion or yield by the reaction equilibrium. Removal of one or both products by a membrane can increase the conversion as the reversible reaction is shifted to the right.

$$A + B \leftrightarrow C + D \qquad (6)$$

Additionally, undesirable side reactions such as the formation of component E in (7) can be avoided by the separation of product C via a membrane. In consecutive catalytic reactions like (8), the desired intermediate product B can be obtained by selective removal of B from the reaction zone. Inhibition effects by one of the formed products, as is often the case in fermentation processes, can be reduced by removal of the products from the reaction.

$$B + D \leftrightarrow E \qquad (7)$$

$$A \rightarrow B \rightarrow C \qquad (8)$$

A comparison between membrane reactors and conventional plug flow reactors can be made on the basis of the two rates governing the latter performance: the reaction rate and the rate of reactant feed per catalyst volume to the reactor. The ratio of these two is the Damköhler number (Da), which also involves tube dimensions. The membrane reactor brings in a third rate constant: the permeation rate of the fastest permeating species. For a comparison between the two reactor types, the Damköhler-Peclet product can effectively be used (DaPe; maximum reaction rate per volume/maximum permeation rate per volume) [67]. For proper performance of a reactor, these three rates will have to be properly balanced. At a too low permeation rate, the membrane has little effect and the reactor behaves like a plug flow reactor, whereas at a too high permeation rate the shell and tube side will equilibrate too quick [68]. Bernstein and Lund [67] recommend $0.1 < \text{DaPe} < 10$ as covering the optimal range.

Gas-phase reactions

Most studies on selective product removal in gas-phase reactions have been focused on hydrogen removal. A detailed summary of the early studies (up to 1994) has been given by Saracco and Specchia [2]. Examples are decomposition reactions (HI and H_2S) [69–71] and relatively simple alkane dehydrogenations. For the dehydrogenation of ethane catalytically active tubular membranes have been used [72], whereas cyclohexane dehydrogenation was performed in packed-bed membrane reactors [73, 74]. Given the industrial importance, the conversion of ethylbenzene to styrene has been studied extensively also [75–78]. More recent studies also focus on hydrogen removal, but tackle more complicated reactions, e.g. the dehydrogenation of propane [79–82], isobutane [83, 84], n-butane [85], methane steam reforming and the water gas shift reaction [86, 87].

From a critical review by Armor [8] a number of problem areas can be defined for the industrial application of dehydrogenation membrane reactors. These are: defects in metallic membranes at elevated temperatures, phase transitions in metallic membranes, leakage, low surface area per volume, severe mass transfer limitations, very low feed flow rates, carbon deposition, and the low turnover number of commercially available dehydrogenation catalysts.

A new development in this field is the use of fluidized bed systems instead of a packed bed. For this purpose, steam reforming of methane has been used as a model reaction [88]. From experimental and theoretical work it can be concluded that fluidized bed membrane reactors potentially represent a promising system as problems of heat transfer and equilibrium limitations can be addressed simultaneously. As one of the major problems encountered is to provide sufficient membrane area per volume, possible solutions are the use of hollow fiber systems [13] or membranes based on microsystem technology. In Fig. 5.7 an indication can be obtained for the potential of this approach to enlarge the effective membrane area versus the superficial area of the wafers used [89].

Apart from the hydrogen removal studies, reactions in which O_2 has to be removed, e.g NO and CO_2 decomposition, are of environmental interest. The membrane materials used for this purpose are mixed oxides such as zirconias [90, 91] and perovskites [92].

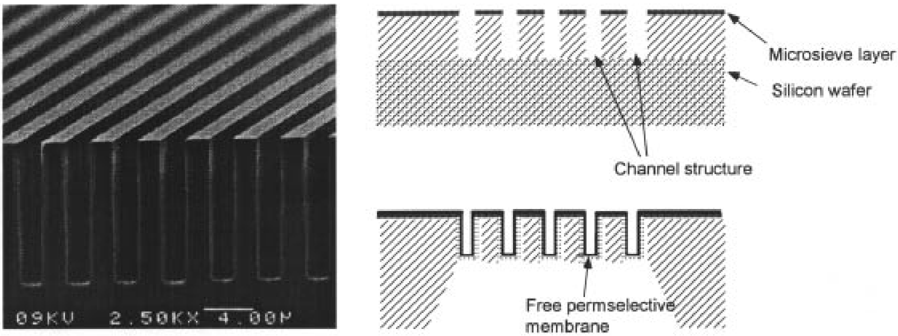

Fig. 5.7: Effective surface area enlargement by vertical etching in a silicon wafer (left). This can be applied to produce high surface area membranes via several deposition and etching steps (right).

Liquid-phase reactions

Reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) can effectively be used to remove one single component or a group of components from a liquid mixture. As an example, a RO membrane has been used in the yeast-catalyzed conversion of glucose into ethanol [93]. The membrane retains the yeast cells as well as the unreacted glucose, thus providing an efficient separation between substrate and product. Ultrafiltration has often been used in enzyme and whole-cell bioreactors [6, 94]. Many systems have been described, including protein and carbohydrate hydrolysis (e.g. starch and cellulose [95]), in which the low molecular weight products are removed through the membrane.

Esterifications and etherifications are industrially relevant chemical reactions. These reactions are often severely limited in conversion, due to an unfavorable reaction equilibrium. In industry, these reactions are forced to completion by adding a large excess of the alcohol, which induces a highly inefficient use of reactor space. Pervaporation has been investigated to remove water selectively from the reaction mixture [96–98], which also avoids the energy-consuming distillation of the excess alcohol. Most of the work published in the literature focuses on the use of polymeric membranes for this purpose, e.g. based on poly(vinyl alcohol) (PVA). Although the principle has proven to be efficient, no large-scale applications have come out until now. The development of processes using ceramic pervaporation membranes, however, seems to lead to industrial applications in the near future [99–100]. This will be discussed in more detail in section 3.1.

5.2.3 Catalyst retention

In the previous sections, a number of catalytic systems have already been described. Here we will summarize the possible roles a membrane can have in a catalytic process. For this purpose, three basic types of catalytic systems can be distinguished (Fig. 5.8 [101]):

a) A membrane can be used to retain a mobile catalyst, thus keeping the catalyst in the reaction fluid. Ultrafiltration and nanofiltration are often applied to retain mobile catalysts such as enzymes, whole cells and homogeneous catalysts.
b) A catalyst can be immobilized in a porous membrane structure. Examples of such catalysts are enzymes and whole cells for biocatalysis and oxides and metals for non-biological synthesis.
c) The membrane itself can act as the catalyst. This form of catalytic system often applies for inorganic membranes such as palladium and zeolite membranes.

As most of the polymeric membranes available are not stable in organic solvents, the main focus of catalyst retention has been in the field of aqueous-phase bioconversions, either by enzymes or by whole cells. This has lead to commercial processes for the production of fine chemicals, e.g. L-methionine or various amino acids (see section 3.4) [102–104]. As most common homogeneous catalysts have molecular weights in the range of 100–1000, this requires the development of solvent-resistant nanofiltration membranes, either polymeric or inorganic in nature. Nevertheless, these membranes can be characterised as “development products”. Therefore, the common solution is to enlarge the homogeneous catalyst, allowing for retention by a solvent-resistant ultrafiltration membrane (e.g. aromatic poly amides) [105]. This has been done for the

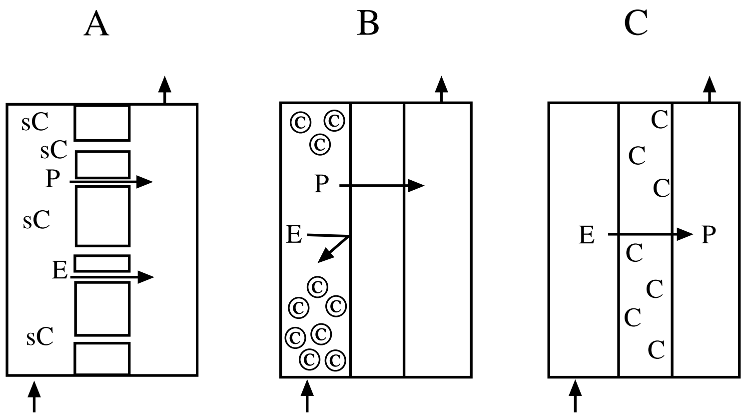

Figure 5.8: Examples of membrane reactors in which the membrane acts in different ways: (a) The soluble catalyst is retained by a membrane, through which products can pass. (b) Selective removal of product by a selective membrane – the immobilized catalyst is present in a fixed or fluidized bed. (c) Catalytically active membrane, where the membrane material itself is catalytically active or the catalyst is immobilized within the membrane [101].

enantioselective addition of diethyl zinc to benzaldehyde using a soluble polymer (a copolymer of 2-hydroxy ethyl methacrylate and octadecyl methacrylate of MW=96000) to enlarge the low molecular weight chiral ligand (a,a-diphenyl-L-prolinol) [106, 107].

5.3 Applications

In this section, several applications of membrane reactors on commercial scale will be highlighted as well as some membrane-based processes which have potential for industrial application. Membrane-assisted esterifications and dehydrogenations will be discussed as well as the OTM process for the production of syngas. Additionally, typical membrane bioreactors such as used in the acylase process developed by Degussa AG, and membrane extraction systems such as the MPGM system and the Sepracor process are described.

5.3.1 Pervaporation-assisted esterification

In industry, esterifications represent an important class of chemical reactions. As esterifications are equilibrium reactions (9), high yields can be obtained by adding an excess of one reactant or by constant removal of the produced water from the reaction mixture in order to shift the reaction to the product side.

$$R_1\text{-CO-OH} + R_2\text{-OH} <-> R_1\text{-CO-OR}_2 + H_2O \qquad (9)$$

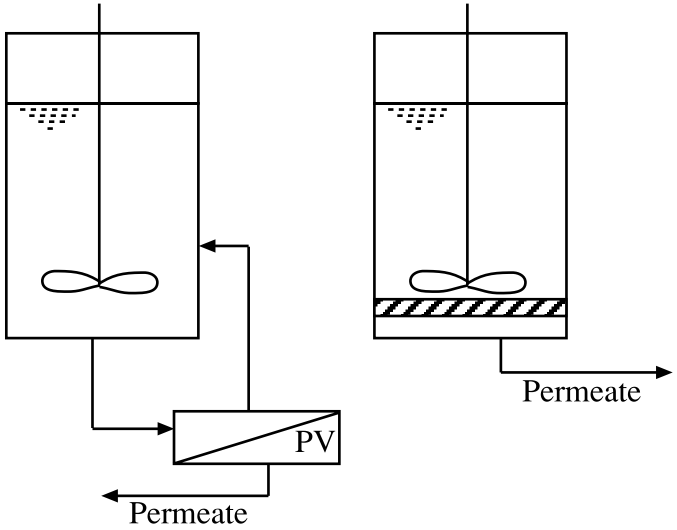

Figure 5.9: Configuration of a pervaporation reactor with an external pervaporation unit (1) and with an internal pervaporation unit (2), respectively [108].

Tab. 5.2: Overview of several pervaporation membranes and their performance for the system water/isopropanol [115]. PSI is defined as the product of flux and selectivity.

Ref.	Membrane type or material	Temp. [°C]	Flux kg/(m^{3}h) 10wt%	Flux kg/(m^{3}h) 10wt%	a (-) 10/ 5wt%	PSI kg/(m^{3}h) 10/5wt%	Comments
109	CMC-CE-01	65	0.11	0.055	370/520	80/30	PSI drops with with increasing temperature
	CMC-CE-02	55		0.09	800	70	PSI increases with temp.
110	Carboxymethylated poly(vinyl alcohol)	80	0.5	0.20	1800/ 3700	900/900	
111	Chitosan (cross-linked)	30	0.15	0.09	1100/ 2000	160/180	PSI is roughly the same at 60°C
113	Sodium alginate	70		1.0	2500	2500	
114	Silica	70		0.3	500	150	
115	Silica	70		2.1	600	1250	after stabilisation PSI=1800

Application of pervaporation processes to selectively separate water from the reacting mixture forms an interesting alternative to conventional distillation, especially in the case of azeotrope formation and low boiling reactants.

Tabl. 5.3: Overview of pervaporation-assisted esterifications, adapted from [14].

Ref.	Reaction	Membrane material	Membrane type	Membrane area [m^2]	Temp. [°C]
116	methanol + acetic acid <-> methyl acetate + H_2O	Nafion	tube	$5.0*10^{-3}$	25
117	ethanol + acetic acid <-> ethyl acetate + H_2O	polyvinyl alcohol	flat cell	1.2	90
117	ethanol + acetic acid <-> ethyl acetate + H_2O	Nafion 117	flat cell	1.2	90
117	ethanol + acetic acid <-> ethyl acetate + H_2O	Nafion 324	flat cell	1.2	90
118, 119	ethanol + acetic acid <-> ethyl acetate + H_2O	polyvinyl alcohol	tube	1.1	80
120	ethanol + acetic acid <-> ethyl acetate + H_2O	polyether imide	flat cell	1.9	75
120	ethanol + oleic acid <-> oleic acid ethyl ester + H_2O	polyether imide	flat cell	1.9	60
121	1-propanol + propionic acid <-> propionic acid propyl ester + H_2O	polyvinyl alcohol	flat cell	2.0	50
122	1-propanol + propionic acid <-> propionic acid propyl ester + H_2O	polyvinyl alcohol	flat cell	2.0	50
122	1-propanol + propionic acid <-> propionic acid propyl ester + H_2O	PSSH-poly vinylalcohol	flat cell	2.0	50
121	2-propanol + propionic acid <-> propionic acid propyl ester + H_2O	polyvinyl alcohol	flat cell	2.0	55
121	2-propanol + propionic acid <-> propionic acid propyl ester + H_2O	polyvinyl alcohol	flat cell	2.0	65
120	2-propanol + propionic acid <-> propionic acid propyl ester + H_2O	polyether imide	flat cell	2.5	85
123	1-butanol + acetic acid <-> butyl acetate + H_2O	polyvinyl acetate	channel reactor	-	155
116	1-butanol + acetic acid <-> butyl acetate + H_2O	Nafion	tube	5.0	25

Both polymer and ceramic membranes are applied in pervaporation-based reactors, for which Fig. 5.9 shows the two basic configurations [108]. Table 5.2 gives an overview of the performance of various pervaporation membranes and Tab. 5.3 shows some examples of membrane-assisted esterification reactions. In addition to these low mole-

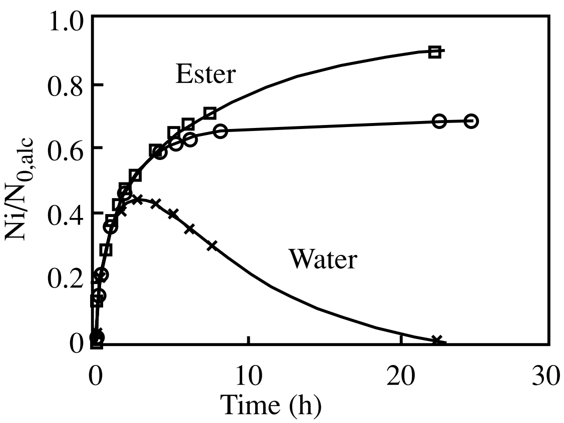

Fig. 5.10: Variation of the molar amounts of ester and water as a function of time for esterification with (□, X) and without (■) pervaporation. N_i: molar amount of component I; $N_{0,alc}$: initial molar amount of alcohol [96].

cular weight esters, pervaporation can also be used for the production of polycondensation esters (resins) [99, 100].

A process performance study has been conducted by David et al. [96] taking the coupling of the esterification reactions of 1-propanol and 2-propanol with propionic acid to pervaporation as a model system. Toluene sulphonic acid was applied as the homogeneous acid catalyst. A poly(vinyl alcohol)-based composite membrane, supplied by Carbone Lorraine-GFT, was used. Fig. 5.10 shows the comparison between the esterification reaction with and without pervaporation. Without pervaporation, the conversion factor reaches a limit, which corresponds to the equilibrium of the esterification reaction. Coupling of the esterification to pervaporation allows the reaction to reach almost complete conversion.

The influence of four different operating parameters on the conversion were evaluated [96], which can be divided into three groups:

- Factors which influence directly the esterification reaction (the catalyst concentration and initial molar ratio)
- Factors which influence the pervaporation kinetics directly (the ratio of membrane area to reactor volume)
- Factors which influence simultaneously the esterification as well as the pervaporation kinetics (the temperature).

For a rapid conversion of lab-scale results into an economically viable reaction-pervaporation system, an optimum value can be determined for each parameter. Based on experimental results as well as a model describing the kinetics of the system, it has been found that the temperature has the strongest influence on the performance of the system as it affects both the kinetics of esterification and of pervaporation. The rate of reaction increases with temperature according to Arrhenius law, whereas the pervaporation is accelerated by an increased temperature also. Consequently, the water content fluctuates much faster at a higher temperature. The second important parameter is the initial molar ratio. It has to be noted, however, that a deviation in the initial molar ratio from the stoichiometric value requires a rather expensive separation step to recover the unreacted component afterwards. The third factor is the ratio of membrane area to reaction volume, at least in the case of a batch reactor. For continuous operation, the flow rate should be considered as the determining factor for the contact time of the mixture with the membrane and subsequently the permeation flux. The catalyst concentration exhibits the weakest influence on the pervaporation-esterification system. The esterification reaction is a first order reaction with respect to the catalyst for both the 1-propanol and 2-propanol esters, in which the apparent reaction rate increases linearly with the catalyst concentration.

The system developed by David et al. [96] shows that application of a membrane process in combination with an equilibrium reaction to continuously remove one of the products formed is an interesting approach to obtain complete conversion of the reactants. For optimization of the process a predictive model has proven to be very useful in order to determine the influence of various operating parameters.

The catalytic esterification of ethanol and acetic acid to ethyl acetate and water has been taken as a representative example to emphasize the potential advantages of the application of membrane technology as compared to conventional distillation [14], see Fig. 5.11. From the McCabe-Thiele diagram for the separation of ethanol-water mixtures it follows that pervaporation can reach high water selectivities at the azeotropic point in contrast to the distillation process. Considering the economic evaluation of the membrane-assisted esterifications as compared to the conventional distillation technique [14], a decrease of 75 % in energy input and 50 % lower investment and operation costs can be calculated. The characteristics of the membrane and the module design mainly determine the investment costs of membrane processes, whereas the operational costs are influenced by the lifetime of the membranes.

Keurentjes et al. [98] studied the esterification of tartaric acid with ethanol using pervaporation. The equilibrium composition could be shifted significantly towards the final product diethyltartrate by integration of pervaporation with hydrophilic poly(vinyl alcohol)-based composite membranes in the process. Based on the kinetic parameters, an optimum membrane surface area could be calculated which results in a mimimal reaction time for the esterification reaction. In the case that the membrane surface area to volume ratio is too low, the water removal is rather slow, whereas at high surface area to volume ratios significant amounts of ethanol are removed as well.

Although low molecular weight esterifications (and etherifications) can benefit substantially from an integration with pervaporation, to our knowledge no large-scale applications have emerged so far. Probably closer to final application is the development by Akzo Nobel on the application of ceramic pervaporation membranes in polycondensation reactions [99, 100]. In the production of alkyd coating resins a mixture of acids, acid anhydrides and alcohols react under the formation of a resin and water. Reaction equation (10) represents a simplified form of this reaction, typically performed at tem-

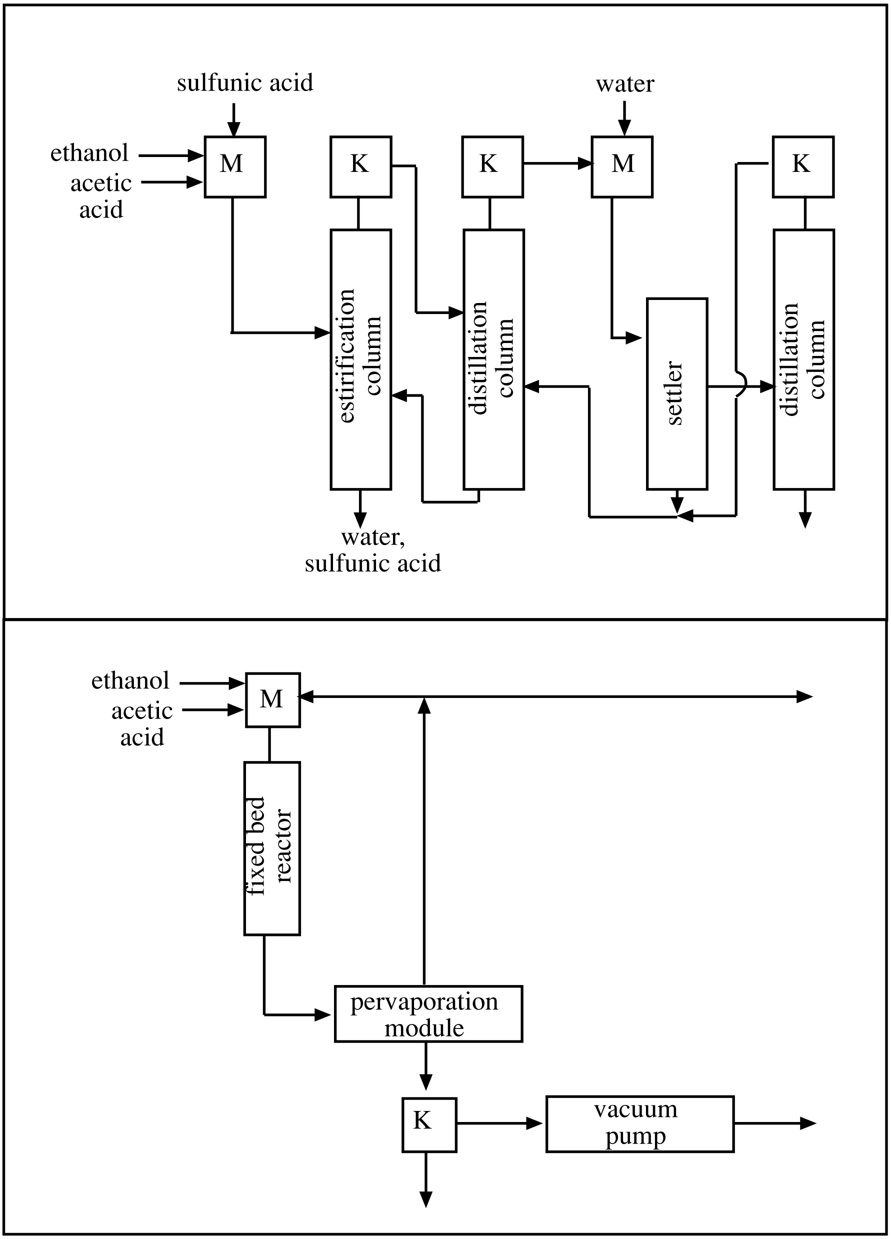

Fig. 5.11: Process scheme of the conventional reaction distillation process (top) versus the membrane-assisted esterification (bottom) for the production of ethyl acetate [14].

peratures between 150 and 300 ºC. The reaction mixture is relatively viscous and in some cases even heterogeneous.

$$R_1\text{-}(COOH)_x + R_2\text{-}(OH)_y \text{ <-> coating resin} + H_2O \qquad (10)$$

With pervaporation membranes the water can be removed during the condensation reaction. In this case, a tubular microporous ceramic membrane supplied by ECN124 was used. The separating layer of this membrane consists of a less than 0,5 mm film of microporous amorphous silica on the outside of a multi-layer alumina support. The average pore size of this layer is 0.3-0.4 nm. After addition of the reactants, the reactor is heated to the desired temperature, the recycle of the mixture over the outside of the membrane tubes is started and at the permeate side a vacuum is applied. In some cases a sweep gas can also be used. The pressure inside the reactor is a function of the partial vapor pressures and the reaction mixture is non-boiling. Although it can be anticipated that concentration polarization will play an important role in these systems, computational fluid dynamics calculations have shown that the membrane surface is effectively refreshed as a result of buoyancy effects [125].

In a kilogram-scale reaction-pervaporation unit, the method has been tested extensively. The applied membranes showed high permeability and selectivity towards water during the whole reaction period. Besides that, the membranes appeared to be thermally and chemically stable for the reaction conditions applied. For this specific application the energy savings as compared to conventional methods are estimated to be more than 40 %, and the reactor efficiency can be increased by at least 30 % [99, 100].

5.3.2 Large-scale dehydrogenations with inorganic membranes

Over the years, several processes for the catalytic dehydrogenation of propane to propylene have been developed, which can be divided into processes based on an adiabatic or an isothermal reactor concept, respectively. The processes currently applied on an industrial scale are based on adiabatic systems, such as the Catofin (Lummus/Air Products) and the Oleflex (UOP) process. As the dehydrogenation of propane to propylene comprises an equilibrium reaction (11), selective removal of hydrogen from the reaction mixture can shift the reaction towards the product side. At high temperatures, thermal cracking may occur.

$$C_3H_8 \text{ <-> } C_3H_6 + H_2 \qquad (11)$$

Van Veen et al. [126] studied the technical and economic feasibility of the application of ceramic membranes in different dehydrogenation processes. As the Oleflex process uses four reactor beds in series, this process is more suitable for implementation of ceramic separation units than the Catofin process, which uses a parallel reactor system. Figure 5.12 shows the configuration of the Oleflex process extended with four membrane modules.

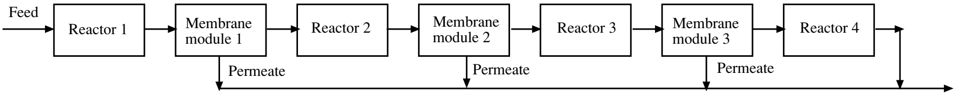

Fig. 5.12: Generalized process flow diagram of the Oleflex process extended with four membrane modules [126].

Based on the adiabatic reactor concept, several configurations of the membrane units have been considered as compared to the conventional Oleflex process [126]. Concerning the technical feasibility, the propane dehydrogenation process requires membranes with a selectivity much higher than Knudsen-diffusion-based selectivity, in combination with a reduced permeate pressure. Additionally, the membranes have to be stable at the working conditions ($T = 650$ ºC, $p = 1.5$ bar) and their performance should be indifferent to coke formation. In an isothermal reactor concept, application of inorganic membranes may lead more easily to a technically feasible process as additional heat for propane conversion is available. However, the difference in price level between feedstock and product is rather small to give an economically viable membrane-assisted dehydrogenation process of propane.

The potential application of ceramic membranes for the dehydrogenation of ethylbenzene to styrene (12) has also been evaluated [126]. In the conventional process, two radial reactors in series are used with one preheater and one interstage heater. Steam acts as an energy carrier and as a diluent.

$$C_6H_5\text{-}CH_2CH_3 \leftrightarrow C_6H_5\text{-}CHCH_2 + H_2 \tag{12}$$

For the dehydrogenation of ethylbenzene in a packed bed ceramic membrane reactor, three configurations are possible using a specific sweep gas in combination with a hydrogen or oxygen selective membrane, see Fig. 5.13.

- The hydrogen permeates through the hydrogen selective membrane tube under the influence of a pressure difference over the membrane. The hydrogen is removed with an inert sweep gas such as steam (A).
- The hydrogen permeates through the membrane and is removed using air as a sweep gas. Subsequently, the hydrogen is burned by the oxygen (B).
- Oxygen permeates through the oxygen selective membrane into the reaction mixture. By oxidative dehydrogenation, the oxygen burns the hydrogen which is formed (C).

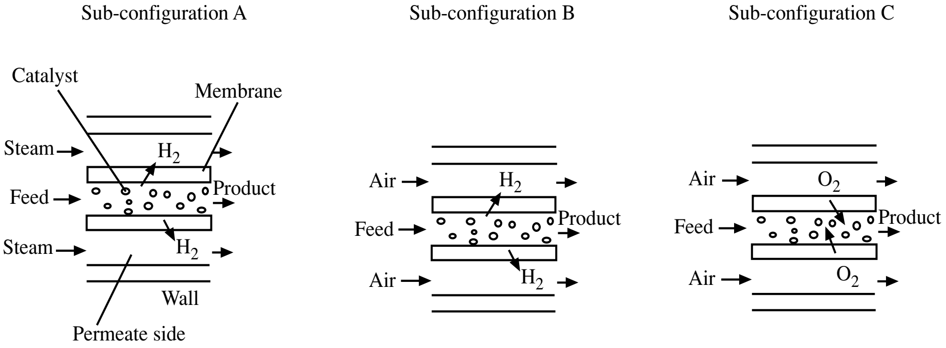

Fig. 5.13: Possible membrane reactor sub-configurations for the dehydrogenation of ethylbenzene [126].

According to the study by van Veen [126], a ceramic membrane reactor does not lead to a feasible process for the dehydrogenation of ethylbenzene. The profit from the higher styrene yield by application of ceramic membranes does not compensate for the expensive membranes. A viable membrane-assisted dehydrogenation of ethylbenzene asks for cheaper membranes, being highly selective with a higher permeability than the membranes currently available.

5.3.3 OTM syngas process

An alliance of five international companies including Amoco, BP Chemicals, Praxair, Sasol and Statoil, has put significant effort into the development and commercialization of a novel technology to address overall cost reduction in the production of synthesis gas (13) [127].

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2 \qquad (13)$$

Conventional processes for the production of syngas involve partial oxidation or steam reforming. In the process with oxygen, an expensive air separation plant is required, whereas in the case of steam reforming high temperature heat additions are necessary.

The alliance is developing the OTM (Oxygen-Transport-Membrane) Syngas process, which integrates the separation from air, steam reforming and natural gas oxidation, see Fig. 5.14. Air is introduced on one side of the membrane, whereas natural gas is added on the other side. Oxygen is separated from air by adsorption on the surface of the membrane where it is subsequently dissociated and ionized. The oxygen ions diffuse through the membrane. The subsequent reaction with natural gas to syngas takes place in the presence of a reforming catalyst at the permeate side of the membrane. High selectivity and high yields are obtained by controlling the oxygen flux through the mem-

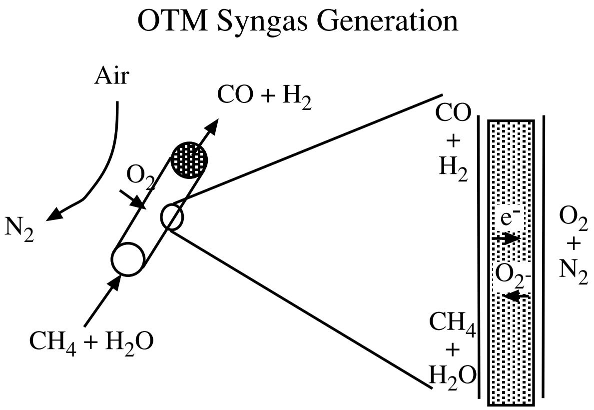

Fig. 5.14: Schematic setup of the OTM syngas process [127].

brane. For the OTM process, dense ceramic materials are used, which are related to inorganic perovskite structures, although no exact details are given on the membranes applied.

The technical challenges of the OTM process comprise amongst others the material performance, fabrication processing-reliability, process integration, engineering-scale-up and cost competitiveness. The alliance participants expect to move the OTM program towards commercialization over the next several years.

5.3.4 Membrane recycle reactor for the acylase process

A particular example of a membrane-assisted process applied on a large scale is the acylase-catalyzed resolution of N-acetyl-D,L-amino acid, as developed by Degussa AG [128, 129]. Annually, the industrial plant produces several hundreds of tonnes of enantiomerically pure L-amino acid. D,L-amino acid is acetylated in a Schotten-Baumann reaction to N-acetyl-D,L-amino acid. Subsequently, the L-amino acid enantiomer is obtained via an acylase reaction. Figure 5.15 shows the reaction scheme.

Regarding the economical viability of the plant, the retention and stability of acylase are essential features for the process. An ultrafiltration unit retains acylase as the mobile catalyst in the reactor. Alternatively, acylase can be immobilized in a fixed or fluidized bed. A mobile catalyst system is preferred compared to the immobilized form, as the mobile catalyst system avoids mass transfer limitations. Additionally, regeneration of the catalyst and scale-up of the reactor are much easier as compared to the process with the immobilized acylase. With respect to the deactivation of the catalyst, the thermal as well as the operational stability of acylase has been evaluated extensively [128, 129]. At a pH of 7, acylase appears to be sufficiently stable for L-amino acid manufacture.

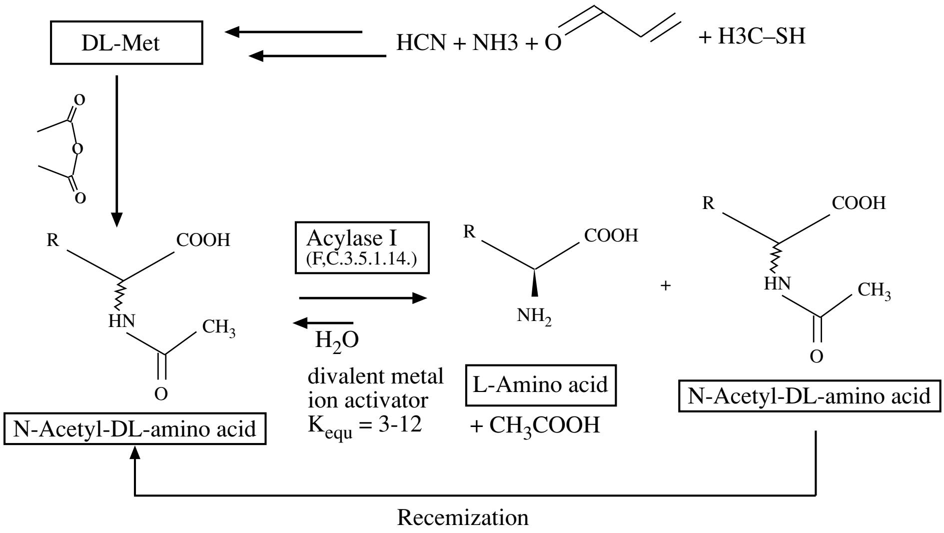

Fig. 5.15: Reaction scheme for the acylase catalyzed resolution to L-amino acid.

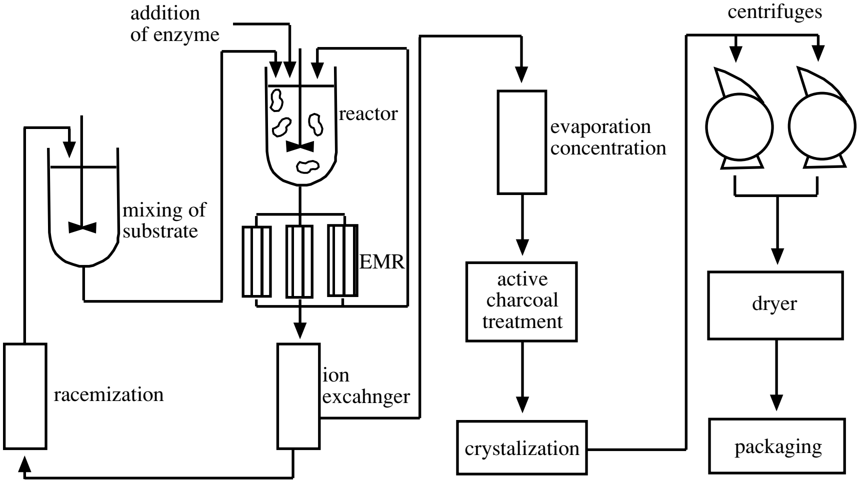

Fig. 5.16: Process scheme of the Degussa acylase process [128, 129].

Figure 5.16 shows the process scheme of the commercial acylase process. In a separation unit of several ultrafiltration modules in parallel, acylase is removed from the reactor outlet stream and recycled to the reactor. Subsequently, the ion exchanger separates the L-amino acid product from the non-converted N-acetyl-D-amino acid, which is racemized and recycled to the reactor.

The acylase process is a typical example of reaction and separation by membranes in a sequential mode. The process is fully developed up to industrial scale, yielding high quality products at good cost effectiveness.

5.3.5 Membrane extraction integrated systems

An example of an industrial membrane bioreactor is the hollow-fiber membrane system for the production of (-)-MPGM (1), which is an important intermediate for the production of diltiazem hydrochloride [130,131]. For the enantiospecific hydrolysis of MPGM a hollow-fiber ultrafiltration membrane with immobilized lipase from Serratia marcescens is used. (+)-MPGM is selectively converted into (2S,3R)-(+)-3-(4-methoxy-phenyl)glycidic acid and methanol. The reactant is dissolved in toluene, whereas the hydrophilic product is removed via the aqueous phase at the permeate side of the membrane, see Fig. 5.17. Enantiomerically pure (-)-MPGM is obtained from the toluene phase by a crystallization step. In cooperation with Sepracor Inc., a pilot-plant membrane reactor has been developed, which produces annually about 40 kg (-)-MPGM per m^2 of membrane surface.

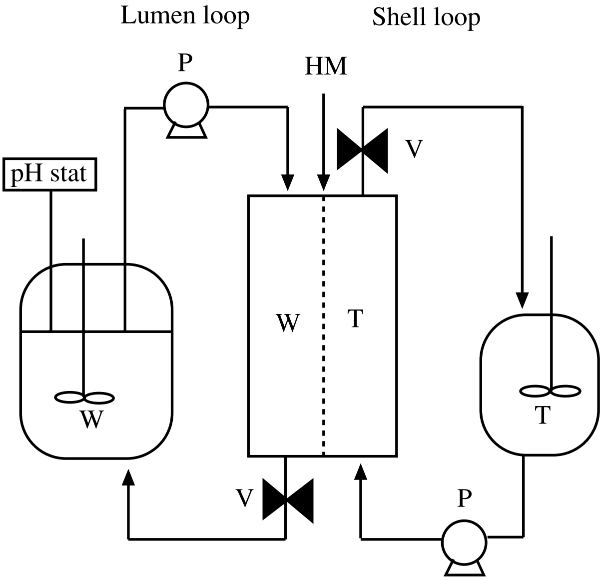

Fig. 5.17: Flow diagram of the membrane reactor for the production of (-)-MPGM. W: water, T: toluene, HM: hydrophylic membrane, P: recycle pump, V: throttle valve.

In a comparable system, (R,S)-ibuprofen can be separated by a membrane reactor [132], see Fig. 5.18. The technique comprises a stereo-specific hydrolysis by an enzy-

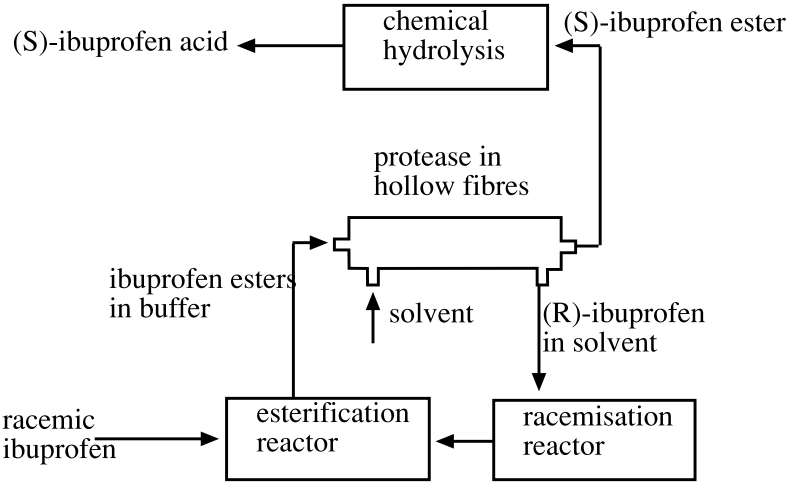

Fig. 5.18: Configuration of the Sepracor membrane bioreactor for the production of (S)-ibuprofen [132].

me. Subsequently, the enantiomeric ester is extracted into the organic phase on the other side of the membrane. In the system developed by Sepracor Inc., (R)-ibuprofen is selectively hydrolyzed by proteases in a hollow-fibre unit and the (S)-ibuprofen ester can be isolated at 100 % yield. This configuration also applies for enantioseparation of other acids such as naproxen and 2-chloropropionic acid.

Although at the moment no large-scale method exists for the production of enantiomerically pure components, it can be foreseen that both the MPGM and Sepracor reactor system have potential for application on larger scale due to their ease of scale-up.

5.4 Concluding remarks and outlook to the future

For the industrial application of membrane reactors, it can be concluded that these are accepted as proven technology for many biotechnological applications. The membranes used in this area can operate under relatively mild conditions (low temperature and aqueous systems). However, there is a tremendous potential for membrane reactors in the (petro) chemical industry, requiring application at elevated temperatures in non-aqueous systems. Often, this will make the use of inorganic membranes mandatory. Especially with respect to the application of inorganic membranes, several key issues need to be addressed in the near future. One of them is the development of high-surface-area-per-volume systems. Potential solutions are the use of ceramic hollow fibers or membranes fabricated using microsystem technology. Long term stability of the membrane materials is a second important issue that will require an ongoing development from the side of materials scientists. A third issue relates to scale up. Firstly, most investigations described in the literature use small (typically 1-100 cm^2) membranes. From past experience in the production of inorganic ultrafiltration and microfiltration membranes it can be expected that the development of a production technology for large amounts of membrane area will require a substantial effort and will probably take several years. Finally, once large amounts of membrane area are available, they will have to be placed in the appropriate modules. The development of these modules will have to comprise several issues. This includes high-temperature sealing, heat transfer and the development of flow patterns avoiding polarization effects, thus allowing for an effective use of the intrinsic membrane properties and the required (not necessarily being the intrinsic) reaction kinetics.

The main part of the developments on membrane reactors for chemical processes has focused on very large scale processes, with emphasis on applications in the petrochemical industry and in the production of bulk chemicals. As described above, many hurdless will have to be taken before implementation on this scale will take place. Although most of the earlier work on membrane reactors has focused on shifting the reaction equilibrium, currently a shift can be observed towards systems aiming on selectivity increase and controlled reactant dosage. As reaction selectivity is of major importance in the production of fine chemicals and pharmaceutical products, it seems plausible to expect that membrane reactors will find their way in the production of chemicals through applications in these areas.

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6 Electromembrane Processes

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List of symbols

m – solution molality,
$\bar{m}$ – molality of Donnan electrolyte,
E – molality of counter ions,
$\theta, \bar{\theta}$ – average molal activity coefficient in solution phase and in solid phase respectively;
$\bar{\chi}_m$ – electric conductivity of ion permeable membrane
$\bar{\chi}_m{}^{//}$ – theoretical electric conductivity of ion permeable membrane based on parallel ion movement model;
$\bar{\chi}_m{}^{\perp}$ – theoretical electric conductivity of ion permeable membrane based on successive ion movement model;
a, b, c, e, and *d* are the parameters of the three-conductor model.
f – is the fraction of gel areas in the ion exchange membrane.
c_0 – constant;
R – molar gas constant
T – absolute temperature.
I_o – total electric current through the membrane;
I_i – the fraction of electric current carried by i-type ions.
$\bar{t}_g$ – counter ions transport number;
$\bar{t}_c$ – co-ions transport number
t_g – counter ions transport number in solution
C_A, C_B – ion concentration for ion type A and ion type B respectively in the releasing solution;
$\bar{u}_g, \bar{u}_c$ – counter and co-ion mobility respectively;
$\bar{a}g, \bar{a}c$ – counter and co-ion activity respectively;
$\bar{\chi}_m, \chi$ – specific resistance of membrane and solution respectively
q_i – quantity of type i ion, gram-equivalent
Q – electric current passed through the membrane, Faraday
K – the maximum possible degree of concentration

m – solutions' ion strength
KCa, KSO_4 – ion ratio in concentrate and dilute flows
$[Ca_2^+], [SO_4^{2-}]$ – the ion concentrations in the feed solution
C_{NaCl} – Sodium chloride concentration in the concentrate
n_g – quantity of water carried with one equivalent of counter ions through a membrane,
n_c – quantity of water carried with one equivalent of co-ions through a membrane.
X – fixed ion concentration in the membrane,
n – kinematic viscosity, cm^2/c
l – distance between the mixing screen elements,
d_o – the thickness of the chamber, cm
h – the height of the mixing screen elements, cm
n_o – kinematic viscosity at 298 K
D, D_o – diffusion coefficient at given temperature and at 298 K
d_m – membrane thickness
α – proportionality factor
$\bar{\gamma}_i$ – fraction of membrane capacity occupied by ions specie i
C_o – bulk solution concentration
i_{lim} – limiting current density
z – ion's charge
C' – solution concentration at the receiving surface of the membrane
K_s – spacer factor
δ – diffusion layer thickness

6.1 Ion exchange membranes

Ion exchange membranes are synthetic membranes permeable to either positively or negatively charged ions in aqueous solution. This unique property makes ion exchange membrane applications very attractive for chemical industry, because it allows for the removal, addition, substitution, depletion, or concentration of ions in process solutions.

The membranes that are selectively permeable to positively charged ions are usually named cation exchange membranes, or simply cation membranes, and membranes selectively permeable for negatively charged ions are called anion membranes. The selectivity occurs due to high concentration if immobile (fixed) ions within the membrane body. Cation membranes have negatively charged fixed ions usually sulfonic or carboxyl groups chemically bound with the membrane's matrix. Their charge is neutralized by positively charged ions (counter ions). An anion membrane would have positively charge fixed ions, usually quaternary ammonium groups, and negatively charged counter ions. Fixed ions and counter ions are connected by ionic bounds in a dry membrane. In the swollen membrane this bond would be dissociated. Therefore, the counter ion is mobile and can be replaced by another ion. Hence the membrane would be permeable to ions with the charge sign opposite to the charge of the fixed ion.

An important feature of ion exchange membranes is their permeability to counter ions and their impermeability to co-ions (ions with a charge like that of the fixed charge). But they are not perfectly impermeable to co-ions. As solvent penetrates ion exchange material some co-ions penetrate the membrane as well, driven by the difference of chemical potentials of solution and membrane. To follow the law of electric neutrality, an additional amount of counter-ions equivalent to the amount of co-ions must move into the ion exchange membrane. This quantity of electrolyte absorbed by this mechanism may be estimated by the Donnan equation, which is based on the law of equity of chemical potentials in both liquid and solid phases. In the case of an electrolyte in which both the anion and the cation have a single charge, and assuming that the membrane's ion exchange capacity is much higher than the equilibrium solution's concentration, the Donnan equation can be written as:

$$^{-}m \sim m^{2}\theta/E^{-}\theta$$

The electric field applied across a membrane would determine the direction of ion movement. Cations move toward the cathode and anions move toward the anode. With the membrane selectively permeable for only cations or only anions, a separation process would take place.

The chemical structures of ion permeable membranes as well as ion exchange resins are three-dimensionally cross-linked polymers with ionic groups attached. The structural units of the most common ion exchange membrane are pictured in Fig. 6.1.

Bipolar membranes have two layers: cation (C) and anion (A) films. Boundary C – A have specific electrochemical property. At current direction C→A electrolyte concentration increases at the boundary. But at the other current direction A→C electrolyte concentration decreases at the boundary to the level at which current transference by hydrogen and hydroxyl ions generated by water dissociation occurs. Low dissociated groups or iron and some other element presence is important for inhabitation recombination of hydrogen and hydroxyl ions. Potential drop only 0.8 V is necessary for modern bipolar membrane performance.

Singly charge selective membranes (also called monovalent selective, but 'valence' should be only for elements) are penetrated most easily by singly charged cations or singly charged anions. These membranes may be synthesized by introducing a barrier layer of oppositely charged fixed groups on the ion permeable membrane surface. They resemble bipolar membranes but the density of the oppositely charged fixed ions (by absolute value) on the ion permeable membrane surface is much less then the density of the fixed ions in the bulk membrane. All counter ions are affected by repulsive forces in this barrier layer, but counter ions with multiple charges are repelled more stron-

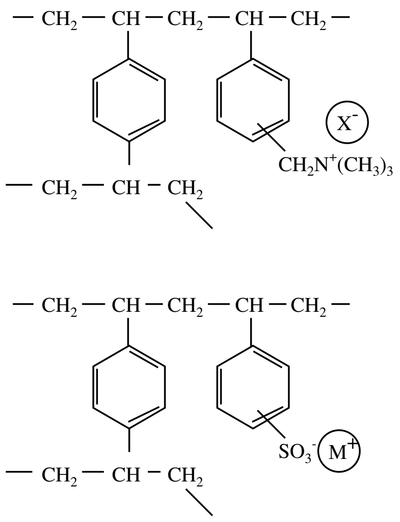


Fig. 6.1: The structural units of the most common ion exchange membrane.

gly. It should be noted that this repulsion is not absolute, and counter ions with multiple charge will carry an increasing fraction of the current through the barrier layer as singly charged ions are depleted from the solution.

Membranes for electrodialysis are typically hydrocarbon films with ion exchange functional groups attached to the polymer chains. Hydrocarbon membranes are usually categorized as homogeneous or heterogeneous. The heterogeneous membranes are made simply by grinding ion exchange resins to a powder, dispersing that powder in a powder of thermoplastic film-forming polymer, applying the powder mixture to a reinforcing fabric, and hot pressing to form a reinforced polymer film with imbedded ion exchange particles. The film-forming polymer is usually polyethylene or poly(vinylidene fluoride), but other polymers could also be used. Typically heterogeneous membranes are thick, opaque and mechanically strong, but they tend to have higher resistance and lower permselectivity than homogeneous membranes, because their ability to transfer ions relies on the continuity of particle-to-particle contact of the ion exchange powder, which is the discontinuous phase in the fused polymer mixture.

The term “homogeneous” is used loosely to describe membranes that are not classified as heterogeneous. On a molecular scale no membrane is truly homogeneous, because the unlike parts of the polymer, hydrophilic ion exchange functional groups and hydrophobic hydrocarbon chains, tend to become segregated into clusters that are much smaller than the dimensions of the resin particles in the heterogeneous membranes.

Typical homogeneous membranes have a polymer matrix of styrene cross linked with divinylbenzene (DVB) and ion exchange functional groups of sulfonic acid or quaternary amines. Manufacture of DVB yields an impure product containing nearly 50 % of ethylstyrene, which participates in the polymerization but does not accept functional groups readily. In some cases the film of styrene-DVB copolymer is made in one step, and the functional groups are added in subsequent steps.

Membranes made with only styrene and DVB tend to have poor physical properties after they are functionalized, so other monomers or solvents are usually added to the formulation before polymerization. Ionics used the approach of adding a non-reactive, high-boiling, water-soluble solvent to the monomers prior to polymerization [1]. Tokuyama mixes the monomers with a plasticiser and PVC powder. This paste is applied to a reinforcing fabric and cured while being held between two release films [2].

Cation exchange membranes are made by adding a sulfonic acid functional group to the benzene ring of the styrene group, usually by treatment with concentrated sulfuric acid, sulfur trioxide or chlorosulfonic acid. Anion exchange groups can also be added to the benzene ring, but a key reagent for that procedure, chloromethyl methyl ether, is a dangerous carcinogen. That danger is avoided by replacement of styrene with chloromethylstyrene and treatment of the polymer with trimethylamine to form a quaternary amine functional group. Alternative monomers for anion membranes include vinylpyridine or methylvinylpyridine, both of which are quaternized with methyl iodide after polymerization [3].

Ion permeable membranes are also made by swelling existing films with styrene and DVB, which can then be post-treated to add functional groups, or by grafting of ion exchange functional groups directly onto the polymer matrix of existing films. For example free radicals formed by radiation of polyethylene or fluoropolymer films become sites for addition of vinyl sulfonic acid, acrylic acid or vinyl amines [4].

The ion permeable membrane properties vital for the electrodialysis efficiency are discussed below.

6.2 Ion exchange membrane properties

6.2.1 Swelling

Ion exchange membrane swelling is determined by the presence of hydrophilic groups in membrane structure. These groups are fixed ions, counter-ions, and co-ions. Water can be found in two states – bound and free. There is no clear distinction between these two states because the molecules are constantly changing their state. And the time a molecule is standing in the same state is far less then 0.001 sec. The most common ion exchange membranes based on styrene and divinylbenzene have hydrophobic matrix. The sulfonic groups serving as fixed ions in strong cation exchange membranes are hydrated with one water molecule. The most common single charge cations are hydrated with 3–4 water molecules. Double charge cations have from 5 to 8 molecules of hydrate water. Anions are hydrated a little. For example, halogen ions are surrounded by 1.5–2.4 water molecules (Tab. 6.1).

Tab. 6.1: Counter ion hydration.

Cation exchange membrane					
Counter ion	H$^+$	Li$^+$	Na$^+$	K$^+$	Rb$^+$
Water content, eq/eq of resin	12.4	12.4	10.6	9.0	8.5
Hydration number	2.7	3.7	3.1	3.0	2.6

Cation exchange membrane					
Counter ion	Cs$^+$	NH$_4^+$	Ca^{2+}	Mg^{2+}	Zn^{2+}
Water content, eq/eq of resin	8.45	11.6	9.7	11.6	12.2
Hydration number	2.0	3.5	4.9	8.0	6.4

Anion exchange membrane					
Counter ion	I$^-$	Br$^-$	Cl$^-$	F$^-$	OH$^-$
Water content, eq/eq of resin	8.4	11.5	13.5	16.0	17.7
Hydration number	1.4	1.7	1.7	2.4	3.0

The ions' hydration increase as crystallographic radius decrease and the ions' charge increase. This effect is very clearly seen for s-elements. The interaction between these elements and water in ion exchange material has electrostatic nature. The metal's cations with filled d-level are capable of forming complexes with water molecules.

The different character of interactions between water molecules on one side and cations and anions on the other side has to be considered. Cations orientated water molecules in order to allow oxygen atoms to form a covalent bond with cations. In case of anions water molecule will face the anion with protons. It is possible to form a hydrogen-type bond in this case.

All kind of membranes have higher moisture content if the counter-ion has higher hydration. The only exception is hydrogen ion, which has special type of hydration. The hydration numbers for counter ions vary widely depending on the method of analysis because different methods have different sensitivity for the interaction between an ion and it's hydration shell. Some membranes can be damaged if they are allowed to dry out, but variation in swelling related to changing the ionic form has little effect on membrane properties.

6.2.2 Electrical conductivity

The electrical conductivity of ion exchange membranes depends on their chemical structure, ionic form, temperature, pH, and solution concentration. Multiple measurements have shown that electrical conductivity χm of ion exchange materials is increasing as swelling, temperature, and counter ions mobility increase and ion exchange constant and counter ions charge decrease. The most influential is the nature of the counter ion. The following rule is always true for a strong ion exchange membrane [5]:

$$\bar{\chi}_m^{I} > \bar{\chi}_m^{II} > \bar{\chi}_m^{III}$$

where I, II and III are the charges of the ion.

There are no known exceptions to this rule for cation membranes. The few exceptions for anions can be explained by higher hydration and by smaller ion exchange constants for the corresponded counter ions.

Multi-charged ions are more trickery for electrodialysis. They have less mobility and can be accumulated in ion permeable membrane reducing its electric conductivity. Multi-charged ions are shielding fixed charges more then single-charged ones. This shielding decreases the transport numbers and reduces current efficiency.

Ion permeable membranes are changing ionic forms during electrodialysis. The electrical conductivity of ion permeable membrane ($\bar{\chi}_m$) containing two ion species 1 and 2 can be calculated as average between two extreme values. One of them is based on the model of parallel independent movement of two types of ions ($\bar{\chi}_m^{||}$) and another one is based on the model of successive ion movement from one fixed charge to another ($\bar{\chi}_m^{\perp}$) [6]:

$$\bar{\chi}_m = \alpha\bar{\chi}_m^{||} + (1-\alpha)\bar{\chi}_m^{\perp}$$

$$\bar{\chi}_m^{||} = \bar{\gamma}_1\bar{\chi}_{1m} + \bar{\gamma}_2\bar{\chi}_{2m}$$

$$1/\bar{\chi}_m^{\perp} = \bar{\gamma}_1/\bar{\chi}_{1m} + \bar{\gamma}_2/\bar{\chi}_{2m}$$

$$\bar{\gamma}_1 + \bar{\gamma}_2 = 1$$

$$\alpha = 2\bar{\chi}_{2m}/(\bar{\chi}_{1m} + 2\bar{\chi}_{2m}) + 2\bar{\gamma}_1(\bar{\chi}_{1m}^2 - \bar{\chi}_{2m}^2)/(\bar{\chi}_{2m} + 2\bar{\chi}_{1m})(\bar{\chi}_{1m} + 2\bar{\chi}_{2m})$$

The membranes in different ionic forms may have very different degree of swelling. In this case the values $\bar{\chi}_{1m}$ and $\bar{\chi}_{2m}$ have to be adjusted to accommodate a decrease in fast-moving ion mobility and an increase in slow moving ion mobility.

Ion permeable membranes are complicated heterogeneous systems. Even ion exchange beads and so-called homogeneous membranes in fact behave as heterogeneous ones. The term "homogeneous" is more likely a historical tradition rather then a term that strictly satisfies the thermodynamic meaning of this term. However the term "homogeneous membrane" is generally accepted. We shall use this terminology keeping in mind its conventionality.

For the purpose of simplicity let us hypothesize an ion exchange membrane as a two-phase system. Each phase is continuous and randomly positioned. Assuming that all fixed ions are concentrated in homogeneous (in the thermodynamic meaning) gel areas. The gel areas are partially in contact with each other and partially separated by inter-gel areas. Assuming also that inter-gel areas do not contain any fixed ions and are filled by equilibrium solution. Electric current can pass by one of three ways: through connected gel areas only (column II), through inter-gel areas only (column III) or through both (column I). Figure 6.2 illustrates this model. Three columns on this picture illustrate three possible current passages. The shaded area would correspond to a gel area. The column width a, b, and c would be proportional to the current fraction passing through a specific passage.

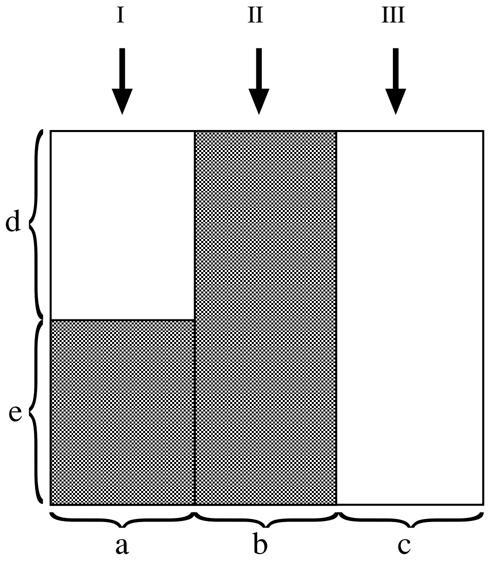


Fig. 6.2: Three-conductor model of ion exchange membrane conductivity.

The electric conductivity of this system can be described by the following formula [3]:

$$K_m = aK_d/(e + dK_d) + bK_d + c$$

$$K_m \equiv \chi_m / \chi$$

$$K_d \equiv \bar{\chi}/\chi$$

The total sum of all fractions should be equal to unity:

$$a + b + c = 1$$

$$e + d = 1$$

The total fraction of gel area (f) in the ion exchange membrane can be express through the model's parameters:

$$ae + b = f$$

The set of equations above are used for calculation of ion exchange membrane conductivity and selectivity versus external solution conductivity.

The counter ion concentration is usually high and reaches up to 3 N in common ion exchange materials. This is the reason for ion exchange membrane's high electric conductance. Donnan exclusion of electrolyte in gel areas determines their weak dependence from equilibrium electrolyte concentration. At the same time electric conductivity of a solution of strong electrolyte is approximately in linear proportion to the concentration up to 1 normal solution. We have to take into account the lower mobility of ions in ion exchange membrane compared to ion mobility in solution due to slowdown by polymer matrix. Therefore, the conductivity of an ion exchange membrane is lower than the conductivity of an electrolyte at moderately high concentrations because of high ion mobility in solution. But ion exchange membrane conductivity is higher than electrolyte conductivity at low concentrations because of the larger number of current carriers in ion exchange membrane. Thus at certain concentration the electric conductivity of ion exchange membrane and equilibrium electrolyte will be equal. This concentration is called the iso-conductivity point. The inter-gel areas in our model do not contain fixed ions or polymer chains. Their electric conductivity must be equal the solution conductivity. So electric conductivity of both gel areas and inter-gel areas must be equal at the iso-conductivity point. The fraction of gel areas f in ion exchange membrane would fluctuate in a narrow range for various ionic forms of the same ion exchange membrane. However we need to note that f will increase as swelling is increasing. For the sodium form of sulfonated styrene-divinylbenzene cation exchange resin and the same type cation exchange membrane the following parameters of the three-conductor model can be used [5]:

Tab. 6.2: Parameters of the three-conductor model.

Parameters	Resin	Membrane	Ion exchange column
a	0.65	0.18	0.25
b	0.35	0.72	0.83f
c	0.00	0.10	0.75–0.83f
d	0.17	0.15	1–0.71f
e	0.83	0.85	0.71f

These parameters can be used for approximate electric conductivity calculation of various ionic forms and various concentrations of equilibrium solution. The conductivity at iso-conductivity point has to be used for both ion exchange resins and membranes.

The electric conductivity of ion exchange membranes increases as temperature rises. This change may be characterized with an equation similar to the Arrhenius equation for viscosity:

$$\bar{\chi} = \chi_0 \exp(-E/RT)$$

The activation energy E is estimated at 21±3 kJ/mol for sulfonated styrene-divinylbenzene cation permeable membranes in equilibrium with one of the following solution: 0.1-1 N NaCl; 0.001-1 N $MgCl_2$; 0.01-0.5 N $CdCl_2$ and 0.1-2.5 N $FeCl_3$. The energy *E* would increase if weakly ionized groups were present in the membrane.

A change in pH has little effect on the electrical conductivity of ion permeable membranes containing strong fixed ions. Membranes containing weak ionic groups may change conductivity sharply with pH change, because the ionic groups in a weak cation exchange membrane have a high degree of dissociation in alkaline solution and the groups in a weak anion exchange membrane are highly dissociated in acidic solution.

Bi-functional ion exchange membranes show two bends on the conductivity versus pH curve. Each bend corresponds to one of two types of functional groups with different dissociation degree at low and high pH values.

Structural factors have large impact on ion exchange membrane’s conductivity. For example increasing of the cross-linking would induce linear decrease of the membrane’s conductivity.

6.2.3 Electrochemical performance

Electrochemical performance of ion exchange membranes is characterized by transport numbers, selectivity and specific selectivity. The ion transport number (t_i) is the fraction of electric current carried by specific ion type:

$$t_i = I_i/I_o$$

For all ions participating in current transport the following expression will be true:

$$\Sigma \bar{t}_g + \Sigma \bar{t}_c = 1$$

The selectivity P can be represented by the expression:

$$P = (\bar{t}_g - t_g)/(1 - t_g)$$

Selectivity demonstrates the relative transport property divergence between real and ideal membranes. Commercial ion permeable membranes typically have selectivity from 0.93 to 0.99.

The specific selectivity of a membrane for ion type A in the presence of ion type B (P_B^A) can be expressed as:

$$P_B^A = \bar{t}_A C_B / \bar{t}_B C_A$$

In the case of a two-component electrolyte the counter ions transport number would be expressed as:

$$t_g = 1/(1+ \bar{u}_c \bar{a}_c / \bar{u}_g \bar{a}_g)$$

The ion activity can be replaced by concentration to a first approximation. The co-ion concentration can be calculated with the Donnan equation based on capacity of ion exchange membrane. It is more difficult to determine the ions' mobility ratio. The counter ion mobility can be calculated based on iso-conductivity point for the appropriate ionic form. The mobility of co-ions can be determined based on self-diffusion coefficient measurement.

The transport numbers can be calculated using the three-conductor model. Co-ion concentration in gel areas of ion exchange membrane is far less then in inter-gel areas, so it would be a valid assumption that co-ions are transported through inter-gel areas only. As it can be easy seen from the picture of three-conductor model the current would be carried only by counter ions in parts a and b. Both counter ions and co-ions would carry the current in part c. Therefore the following equation would describe the transport number of the counter ion in the membrane:

$$\bar{t}_g = 1 - t_c c/K_m$$

$$K_m \equiv \bar{\chi}_m / \chi$$

For practical purposes the most common characteristic of membrane electrochemical performance is current efficiency, which is defined as current fraction η carried by a specific ion type i.

$$\eta_i = q_i / Q$$

The major difference between transport number and current efficiency is that the latter characterizes total transport through the membrane including diffusion. (Diffusion is suppressed during experimental determination of transport numbers.)

6.2.4 Diffusion permeability

Electrical conductance of ion exchange membrane $^{-}\chi_m$ in various ionic forms can be used for an approximate estimation of ions' self-diffusion coefficients D_i using Nernst-Einstein equation:

$$D_i = \frac{RT}{z_i F}\frac{\chi_m t_i}{E}$$

The diffusion coefficients calculated this way is usually higher then values measured by independent methods. It can be explained by the fact that during the self-diffusion measurements ions are moving toward each other and the water present in the ion exchange resin is motionless. At the time of electric conductance measurements all counter ions are moving in one direction and create electroosmotic flow. It is obvious, that in this case the ion's movement would have less resistance as they move along with the liquid flow.

The counter-ion diffusion coefficients obtained by kinetic study or by conductivity measurements cannot be used as membrane diffusion coefficients, because counter ions and co-ions are moving in opposite directions in electrodialysis. However co-ions are motionless at the time of ion exchange between equal activity solutions. Therefore the ion migration conditions are totally different in these cases.

It should be noted that ion exchange membrane swelling depends on external solution concentration. This fact has a significant impact on membranes' diffusion permeability. Moreover, the real life situation often includes an ion exchange membrane facing a concentrated solution on one side and a dilute solution on another side. A concentration gradient occurs within the membrane and affects it's diffusion and osmotic permeability.

By the order of magnitude the diffusion permeability of commercial membranes is about 10^{-6} cm^2 s^{-1}.

6.2.5 Hydraulic permeability

Hydraulic permeability is measured as volume of liquid passed through one unit of membrane surface for one time unit at the one unit of pressure difference. For most commercial membranes this parameter has value 10^{-10}–10^{-11} cm^3 g^{-1}s^{-1}.

Water can penetrate through either gel areas or inter-gel areas in homogenous membrane. The inter-gel areas are less cross-linked, and the water flow would meet less resistance in these areas. However the volumetric fraction of inter-gel areas is small; therefore, it is not possible to predict the contribution of gel areas and inter-gel areas in total hydraulic permeability.

In heterogeneous membrane water can penetrate through ion exchange particles, through gaps between them, and through binding polymer. The pore radius estimation and comparison of water transfer coefficients with water self-diffusion coefficients suggests that all three transports take place.

The external solution concentration has an opposite effect on the membranes hydraulic permeability for homo- and heterogeneous membranes. As solution concentration is increased the hydraulic permeability of a homogenous membrane decreases because water penetrates mostly through the gel of homogeneous membranes, because the gel area progressively dehydrates as solution concentration increases. In case of heterogeneous membrane the water is passing mostly through the cracks between the gel areas and bounding polymer, and these cracks enlarge as the solution concentration increases, because of shrinkage of the resin particles.

6.2.6 Osmotic permeability

The osmotic permeability of ion exchange membranes D_{osm} can be estimated by comparing self-diffusion coefficient of water in the membrane D_w for various degrees of hydration of the membrane. As water content increases (up to 4 mole of water per equivalent of fixed ion) the water molecule mobility increases, rising steeply at the beginning and more gradually latter. It also rises with increasing crystallographic radius of the counter ion.

The nature of the membrane matrix has significant influence on water mobility in the membrane. Water diffusion coefficients are high in perfluorinated membranes with weak hydrophilic interaction [6]. The coefficients are lower for membranes with hydrocarbon matrix with stronger hydrophilic interaction. A correlation exists between self-diffusion coefficients of water and co-ions: the water self-diffusion coefficient increases as co-ion self-diffusion coefficients increase. It is possible that co-ions migrate in swelling water along the pore axis.

As the solution concentration increases, the osmotic permeability of heterogeneous membranes increases linearly and the osmotic permeability of homogeneous membrane decreases logarithmically. A membrane in single-charge ionic form would have the osmotic permeability approximately twice as high as the same membrane in double-charge ionic form. The order of magnitude of D_{osm} would be about 10^{-5} cm^3 sec^{-1}.

6.2.7 Electroosmotic permeability

As transport numbers can characterize ion transport through a membrane, a water transport number t_w can be assigned to characterize solvent carried through a membrane. This number would express a number of moles of water carried through the membrane with one Faraday of electrical charge.

$$\bar{t}_w = n_g \bar{t}_g - n_c \bar{t}_c$$

The solvent transport number is not a characteristic of a membrane or a specific pair of ions. It can have either linear or non-linear dependency on $\bar{t}_g$ because this characteristic would depend on the degree of membrane's heterogeneity, current density, the nature of the polymer matrix and the nature of the ion. It was determined for cation membranes that the solvent transport is higher when a counter ion's hydration number is higher.

Higher solution concentration leads to lower electroosmotic flow through a homogeneous membrane with water content over 19 %. This effect is more pronounce if the counter ion is more hydrated, and it can be explained as increasing electrostatic interaction in the gel phase of the ion exchange membrane concurrent with decreasing pore radius. In case of heterogeneous membranes and homogeneous membrane with water content less then 19 %, the electroosmotic flow is independent of the solution concentration. The explanation of this effect is connected with the inner structure of the ion exchange membrane in a way similar to the hydraulic permeability.

The electroosmotic permeability increases with the increased swelling. The nature of fixed groups and ion exchange capacity is negligible. Also the membrane nature has little influence in case of highly cross linked structures with equal hydration numbers. However for low cross linked membranes the characteristic $\bar{t}_w$ would have a higher value in the case of hydrophobic matrix rather then in the case of hydrophilic ones. For example perfluorinated membranes have higher electroosmotic coefficients then membranes based on hydrocarbon matrix. Not all water in a membrane moves with counter ions. It was determined that only 75 % of total water content is moving in a perfluorinated membrane, 60 % – in a polystyrene based membrane, and 33 % – in a polyacrylic based membrane. The membrane electroosmotic permeability has magnitude of 10^{-3} cm^3 A^{-1} sec^{-1}.

6.2.8 Polarization

The electric current is carried predominantly by only one kind of ion in an ion exchange membrane – by cations in a cation membrane and by anions in an anion membrane – in contrast to the case in free solution where both kinds of ions carry current. Therefore concentration changes take place in the solution close to the membrane surface. These changes are called concentration polarization.

Let assume that there is a thin non-mixed solution layer near the membrane with thickness δ. The concentration in this layer would change linearly from the bulk concentration C_0 to the concentration C_1 on the membrane surface. Let us disregard the electrolyte diffusion on the opposite side of the membrane. Than it is obvious, that at certain current density the concentration would approach zero on the receiving membrane surface. This current density is named limiting current density ilim and it can be described by the equation:

$$i_{lim} = DC_0F/\delta(\bar{t}_g - t_g)$$

Taking into account the electrolyte diffusion on the other side of the membrane, the equation should be [5]:

$$i_{lim} = (D/\delta + 4\ {}^{-}DC/Xd_m)zFC/\ ({}^{-}t_g - t_g)$$

In case of free convection:

$$\delta \sim [D\eta/(C_0\text{-}C')]\ {}^{-}$$

In case of laminar flow

$$\delta \sim v^{-} - \eta^{1/6}\, D^{1/3}$$

In case of turbulent flow passing through chamber with mixing screen the thickness of diffusion layer can be described [5]:

$$\delta = 0.0685\ K_s\ [D_0T\ [1 + 0.0158(T - 298)]]^{1/3}\ (ld_o)^{0.25}\ (1 - h/d_o)^{0.5} / v^{0.5}$$

For the practical purposes the relation between the limiting current density and flow velocity can be approximate:

$$i_{lim} = Av^n$$

The empirical coefficients A and n can be determined from current-volt curves. Several researchers reported n = 1/2 independently from the flow profile. It is possible to calculate that coefficient n = 1/2 in the case of uniform flow profile. The theoretical value for the case of parabolic flow distribution is one third. It is in a good agreement with experiment:

Coefficient	Theoretical value	Experimental value
A	1.05	0.96
n	0.33	0.34

We have to note that calculated electric resistance of an electrodialysis compartment based on polarization curves is somewhat higher then experimental ones across all flow rates. It may be explained by influence of volume charge, concentration, heat, and natural convection on the polarization characteristic.

The method of laser interferometry allows measurement of concentration in the narrow boundary layer with resolution up to 2 micrometer. The results of these measurements are expressed as an empirical equation linking diffusion layer thickness and flow velocity:

$$\delta = 2.1\ 10^{-2}\ v^{-0.5}$$

These measurements demonstrated that as current approaches the limiting current, the concentration is decreasing but it never descend below one half of the bulk concentration. These measurements also reveal a non-linear concentration profile in diffusion layer at the current density below the limiting one. Convection occurs near a cation membrane surface at the current density high than the limiting. This convection levels the concentration at the thin boundary layer. However there is no convection flow near anion membrane at the current exceeding the limiting one. Therefore the concentration in the diffusion layer decreases to very low values.

An increase in membrane uniformity leads to a higher limiting current. The membrane surface condition has noticeable influence on limiting current value. The polarization characteristic may deteriorate as a result of fixed ion concentration reduction due to ion exchange membrane degradation at the time of manufacturing or at the time of operation, or adsorption of low mobility organic substances present in solution or leached from the membranes.

Desalination of very diluted solutions is done in electrodeionization apparatus (please refer to paragraph 6.3.2). The desalination compartment of electrodeionization stack is filled with granular or fibrous ion exchange material. Such packing not only lowers electrical resistance of desalination chambers, but also improves current efficiency. Conductivity of the system the ion exchange resins – solution can be calculated on the equation of three-conductor model using volume-average conductivity of the cation and anion resin mixture. The course of an electrical current through system of mixed ion exchange resin – solution is associated with some features, which are not observed in case of individual resin [7]. Assuming random distribution of anion (A) and cation (C) exchange granules four types of granule connection can be distinguish along the electric currents direction (→): two cation exchange granules (C→C), two anion exchange granules (A→A); and contacts between two unlike granules (C→A, A→C). Let's examine processes on each type of contacts during the current passing. Each pair of granules has both direct contact and contact through thin layer of electrolyte between them. In case of the two cation exchange beads C→C cations are crossing over from the left bead to the right one either through the area of direct contact or the solution between the granules. The electric current running through this pair does not generate any concentration change neither on the boundary itself nor in the surrounding area. The similar situation is near the A→A type contact. The only difference is the opposite direction of the current carrying ion movement. On the boundaries C→A and A→C the swapping of current carrying ions takes place. The swapping from cation conductivity to anion conductivity on the C→A type contact is associated with ion accumulation, which means increasing of solution concentration. On the contrary, swapping from anion conductivity to cation conductivity on the A→C type contact leads to ion withdraw into the granules and reduction of solution concentrations. As concentration decreases to a very low level "water-splitting" phenomenon occurs. This phenomenon represents splitting a water molecule into hydrogen and hydroxyl ions. Sometimes this phenomenon is also called as acid-alkali generation.

For more detailed learning of ion transport and polarization phenomena the monograph [8] is recommend.

6.2.9 Chemical and radiation stability

Mostly ion exchange membranes are composite materials. Because of this, their chemical, thermal and radiation stability is determined not only by stability of the separated materials but also by the changes that occur at the phase boundaries. The latter is especially important for heterogeneous membranes because of damage to the bonding between high molecular polyelectrolyte and film forming polymer as well as delaminating of the reinforcing fabric.

There are notions that ion exchange membrane based on polystyrene and polyethylene are stable in 30 % HCl and 25 % NaOH as well. But it has been reported that membrane selectivity decreased monotonically during their heating in water at 80°C, which may be explained by expansion of membrane pores filled with external solution.

During exposure of ion permeable membranes to radiation, their mechanical firmness and flexibility decreases. Ion exchange capacity, cross-linking, conductivity and selectivity decrease as well.

Application of the three-conductor model allows the estimation of the scale of porosity increase during exposure of ion permeable membranes to radiation. The first portion of radiation increases porosity significantly; subsequently porosity changes a little. But changes in swelling indicate macromolecule destruction with higher radiation doses. Reinforcing ion permeable membranes does not improve their radiation stability significantly. For example mechanical firmness of swelled ion exchange membrane based on polystyrene and polyethylene decrease to half their original value at 80 Mrad. At 200 Mrad they cannot be used at all because they may be destroyed by slight bending.

Interestingly perfluorinated membranes have superior chemical stability, but their radiation stability is worse than that of membranes with hydrocarbon matrix.

6.3 Electromembrane process application

6.3.1 Electrodialysis

Electrodialysis (ED) is used to remove ionized substance from liquids through selectively ion permeable membranes. ED is the most widely commercialized electromembrane technology. Desalination of brackish water is the area of electrodialysis application with the largest number of installations. This chemical-free technology competes with reverse osmosis. Electrodialysis shows better resistance to fouling and scaling. It also has an economical advantage in desalination of low salinity solution [9]. Also it should be kept in mind that because of small material consumption ED is the most environmental friendly process for solution desalination [10].

Electrodialysis has the ability to concentrate salts to high levels with much less energy consumption than evaporation would require. That capability has been utilized in Japan to make edible salt by recovering NaCl from seawater and concentrating it to 20 % before evaporation. The plants there are huge; some have greater than 100,000 square meters of membrane. Salt recovered by electrodialysis in Kuwait is the raw material for a chlor-alkali plant there. Electrodialysis has also been used to concentrate salts in reverse osmosis brines [11].

Electrodialysis is used in a wide variety of food applications. Throughout the world it is used to remove salt from cheese whey so that the other components of whey can be used as food for humans and animals. In Japan the mineral composition of cows milk intended for infant formula is altered by electrodialysis to more closely resemble the composition of mother's milk. In France potassium tartrate is removed from wine to prevent its precipitation. In Japan salt is removed from soy sauce to allow its use by people with hypertension. Salts of organic acids, e.g. lactic and succinic, produced by fermentation are recovered from the fermentation broth and concentrated by electrodialysis [12]. Amino acids made by synthesis or by hydrolysis of proteins are desalted at their isoelectric pH.

In the food applications mentioned above it is impractical to remove components that could foul the membranes, because those are necessary constituents of the product. In such cases the process is operated under conditions that minimize fouling, and then the fouling that does occur is handled by cleaning in place (CIP). The CIP procedures can include soaking in brine, current reversal and washing with acid, base and non-ionic surfactants.

The mandatory condition for an electrodialysis process to be executed is an alternating order of cation and anion membranes and electric field applied across the entire assembly (Fig. 6.3). Between the alternating membranes are two types of compartments – desalination and concentrating. Ions will migrate from the compartments where electric current is passing from an anion membrane to a cation one (the even compartments on the Fig. 6.3). They will be transferred to the successive compartments (the odd compartments on the Fig. 6.3). These compartments will accumulate the ions because the ion exchange membrane between them would prevent ions from moving further. Therefore the solution in the even compartments will be demineralized and solution in the odd compartments will be concentrated.

The solution is alkalized in the cathode compartment and it is acidified in the anode compartment. As a result the entire flow incoming to the electrodialysis apparatus can be separated into desalinated and concentrated streams. Co-ions absorbed by the membrane reduce the efficiency of this process. The highest possible degree of concentration can be achieved if the no incoming solution is supplied to the concentrated compartments. In this case water would be delivered to the concentrate compartments by osmosis and electroosmosis and in the hydration shells of the transported ions.

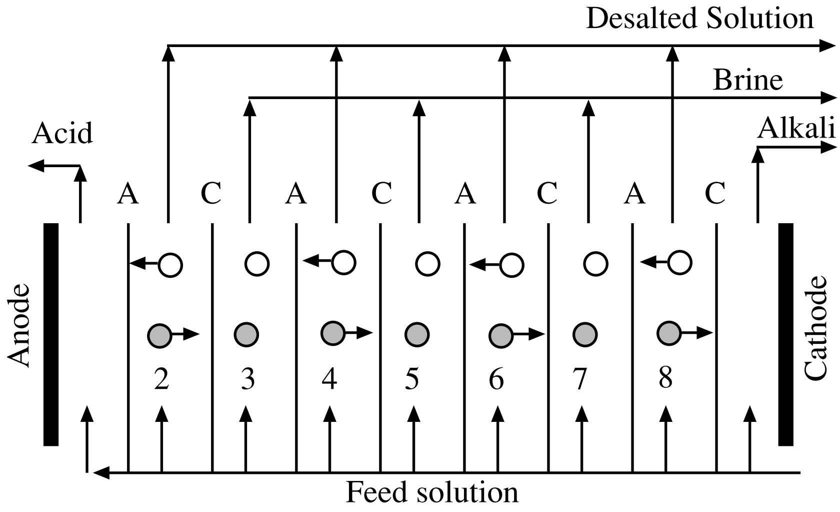


Fig. 6.3: Arrangement of membranes for electrodialysis.

The electroosmotic phenomenon makes it possible to use electrodialysis for concentrating uncharged substances, which would not normally migrate in an electric field. For example by adding a dry electrolyte to a non-electrolyte solution and then desalting it in an electrodialysis apparatus it is possible to remove a considerable portion of water from the original solution. Water will be moved by electroosmosis from desalination compartments to concentrating ones.

There are several common elements in the design of any electrodialysis stack: end blocks, end frames with electrodes, membranes, spacers between membranes, and manifolds for inlet and outlet of fluids. The electrodes used in an electrodialysis stack must withstand the electrochemical reactions and the solutions that circulate within the electrode chambers, as well as to the electrolytes, which are carried there due to electrodialysis and form as a result of electrolysis. Residue must not be formed inside the electrode chambers, while the chamber itself must be thin enough to not create too much resistance to the electric current.

Titanium covered by platinum or by dioxide of manganese, ruthenium, iridium or other substances is most commonly used as an anode. Graphite and graphite covered with lead dioxide have also been used as anodes. Under some conditions, high pH and absence of salts in the anolyte, nickel can be used as the anode. Stainless steel is commonly used as the cathode. If current reversal is employed, the same material, platinized titanium or graphite, is used for both electrodes. Electrode chambers should be flushed with large flow of rinse solution in order to remove the electrode reaction products.

Special spacers are used for membrane separation. Along with membranes, spacers are important structural parts of the electrodialysis stack. In fact, the type of spacer used usually dictates the design of the electrodialysis stack. In electrodialysis, the spacer regulates the distance between the membranes and guides the flow of fluid in a certain way. The spacer is usually made of non-conducting and hydrophobic materials, elastic enough to conform to and form a seal with the membrane and yet rigid enough to not be pushed out from the stack at the time of stack tightening. Materials such as polyethylene, polypropylene, polyvinyl chloride, and various elastomers are used.

In normal electrodialysis the spacers are made of non-conductive material. However, ion-conducting spacers are used to receive extremely desalinated water. Depending on design, the fluid between the membranes can move through channels, which form either a tortuous path or a set of parallel paths.

In a tortuous path spacer, the flow of fluid changes direction several times and gains large speeds due to lathes attached to the walls. In order to prevent the displacement of these lathes, they are fastened by crosspieces, which are thinner than the spacer is. The use of the crosspieces also allows whirling of the flow of fluid and lowering the concentration polarization. For better whirling, crosspieces should be located at angles of 15–75 degrees to the flow. Tortuous path spacers are made by die-cutting sheets of polymer to form lathes, ribs and a peripheral gasket. Two pieces of slightly different configuration are glued together to form a single unit. These spacers are easy to manufacture, but they significantly obscure the surface of the membrane.

Spacers for parallel path flow usually consist of two elements – a peripheral forming the outside walls of the chamber, and a separator, which is nested inside the gasket. The spacers for the desalination and concentration chambers are often identical. Potential drawbacks of such a design are poor flow distribution and stack deformation. To increase the stability of the design plastic guide rods can be put through the gaskets and membranes.

Some separators are made of crimped perforated sheets and sheets modified by the break-and-stretch method. These separators are easy to make, good at whirling the fluid, but significantly mask the membrane.

Netting separators, which appear as two layers of parallel filaments fused at the crossover points, have smaller footprint on the membrane surface. Vexar non-woven netting, developed by DuPont but now made by many others, the most commonly used separator in parallel path electrodialysis stacks. These separators can be made by extrusion of a variety of polymers.

The electrodialysis reversal systems with netting-based spacers (Fig. 6.4) have higher efficiency and lower energy consumption. Non-woven netting is better turbulence promoter. This leads to higher limiting current density and better ion transport through the membranes. However it also results in higher hydraulic resistance of the desalination channel [13].

Depending on the hydraulic scheme of connection all electrodialysis apparatuses can be separated into single-pass and circulating. Circulating apparatuses can be of periodical and continuous types. Single-pass apparatus could be single-stage or multi-stage. In each stack the feed can be parallel or successive. As the fluid is desalted, the critical speed of the flow should be increased. Therefore multi-stage arrangements have advantages because the number of chambers can be decreased at each subsequent stage. Desalted solution goes through the compartments successively, and its speed increases. Thus, all compartments provide optimal conditions for desalination. In some cases, it is most rational

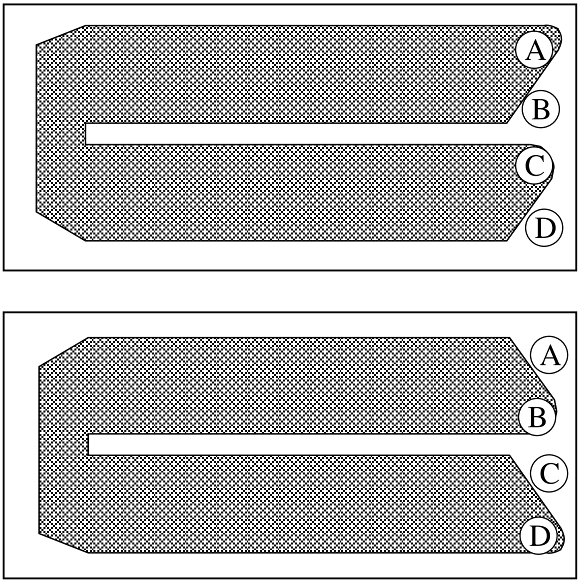


Fig. 6.4: Demineralizing (top) and concentrating (bottom) spacers. A, B, C, D are the openings in the spacer forming flow passage through EDR stack.

to connect desalination chambers or packets in sequence and concentration chambers in parallel. The common disadvantage of all devices with a successive distribution of flows is the significant change in pressure from one chamber to the next, which could cause chambers to collapse with contact between or even tears in the membranes.

Counter-flow feed of desalination and concentration compartments might be considered as a way to decrease the diffusion transport of salt and increases the output of electrical current. Electrodialysis efficiency would increase, but pressure difference between chambers would be higher than with parallel flow. That is why, in practice, the parallel system of solution flows in neighboring chambers is preferred, disregarding its higher energy demands. A parallel flow within a single stack and counter flow within stack sequence is a practical solution for a large-scale commercial system.

Also done on a small scale is the flow arrangement in crisscrossing directions with a parallel connection of the same kind compartments.

The most commonly used method of solution feed to a filter-press type electrodialysis stack is through matching openings in spacers and membranes, which in an assembled state form manifolds along the length of the stack. The channels are connected with the insides of the appropriate compartments. Common disadvantages of all filter-press type stack designs are the passage of electric current (called shunt currents) through the manifolds and the possibility of cross-leak of liquid between the manifolds of desalination and concentration solutions.

Scaling and fouling can cause serious operational problems in electrodialysis. Precipitates in an electrodialysis apparatus have low specific conductivity that can substantially increase electric resistance of the membrane and the whole apparatus. Consequently it leads to increase in specific energy consumption per unit of product and to local heating. Sometimes the heating may be so significant that result in membrane melting, cell's leakage and cross-leak. Because they cause local distortion of current and solution flow, precipitates tend to spread from the point of their origin. The precipitate's origin can be one of the following: electrophoretic deposit of solid particles suspended in solution; increasing of ion concentration above the solubility limit, and pH change in the boundary layer. The precipitation occurs more often in concentration cells where the concentration on ions capable of forming low solubility compounds reaches the maximum.

The maximum possible degree of concentration K can be calculated with the following formula [14]. This formula takes to account selectivity of ion transport through the membranes for the concentrate's ion strength m from 2 to 6.5.

$$K \leq \left(\frac{2.910^{-3}\mu}{C_{NaCl} K_{Ca} \left\{ Ca^{2+} \right\} K_{SO^4} \left\{ SO_4^{\ 2-} \right\}} \right)^{0.5}$$

Also it is very convenient to use Langelier Index [15].

The danger of precipitate formation is especially high if current density is above the limiting value. At this condition current is carried by ions from the dissociation of the solvent. In water solution they would be the hydrogen and hydroxyl ions. The pH will rise in the boundary layer near the cation membrane on the side facing desalination cell and near anion exchange membrane on the side facing concentration cell. The rising pH can reduce the solubility of some solutes. Practically the most common precipitate is calcium carbonate:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

$$Ca^{2-} + CO_3^{2-} \rightarrow CaCO_3$$

The scale usually is confined on ion exchange membrane surface. The reason for the local sediment growth is the concentration fluctuations. The concentration fluctuations are the results of non-uniform flow distribution in the cell.

More often the sediment contains carbonate and hydroxide. Therefore the most common method to remove the sediment is concentrate acidification or current reversal [16]. Electrodialysis reversal (EDR) is an electrodialysis process with periodic reversal of the electric field. As the direction of electric current is switched desalination chambers become concentrating ones and vice versa. Colloidal and organic precipitate accumulates in desalination chamber. As this chamber become a concentration one after switching the current direction, the organic or colloidal precipitate is washed away with concentrate flow.

Fouling of ion permeable membranes is often connected to the presence of weakly ionizable organic substances in the process solution. The organic ions produced by these substances have low mobility in the membrane phase, so they concentrate at the membrane-solution interface. Eventually these ions are absorbed by the membrane, which leads to membrane poisoning.

Current reverse and regular acid/base treatment will not completely restore the original polarization characteristics. Visual observation with a microscope may reveal "pickling" on the membrane surface. Mechanical renewal of the membrane surface would help to restore the original polarization characteristics. However the properties are changed irreversible if degradation penetrates deep into the membrane. Cation membranes are usually more stable then anion membranes. Alkaline environment accelerates membrane degradation. A process of "self-poisoning" takes place. For example an alkaline extract from anion membrane added to the solution treated by electrodialysis would cause 30–40 % reduction in limiting current, and 7-8 fold increase in polarization, reaching 8–9 volts at a current density twice the limiting value.

Deteriorating strongly ionized groups can transform into weakly ionized groups. Weakly acidic and weakly basic groups would have low degree of dissociation in neutral solutions or at the current density close to the limiting one.

Microflora can form an inhibiting film on the membrane surface. This film increases the membrane's surface resistance and decreases the limiting current density.

Electrodialysis of a solution containing organic matter has additional complications. Organic substances may decrease the limiting current density due to concentration profile changes in the diffusion layer as well as due to forming a fouling film on membrane's surface. For example the presence of polystyrene sulfonate in potassium chloride solution at the time of electrodialytic treatment leads to decrease of potassium and chloride ions concentration and increase of polystyrene sulfonate ion concentration in the diffusion layer. In the presence of the negatively charged organic ions the chloride transport in a solution decreases and limiting current density falls. The same effect causes reduction of membrane selectivity due to ionic group blocking by organic ions.

A significant reduction of limiting current density can be caused by formation of a surface polarized membrane-fouling film of macromolecules or colloidal substances. Fouling film can be electrical neutral, or with the fixed charge like the fixed charge of an ion permeable membrane. The film may comprise unreacted intermediates and byproduct of membrane synthesis or their decomposition products. The presence of a porous film is an explanation for different transport numbers of hydrogen and hydroxyl ions through the membranes at the current density above the limiting value.

Weakly ionized organic substances have very low mobility in the membrane. Therefore they accumulate near the membrane-solution interface where they are absorbed by the membrane and result in membrane fouling. The large intensity of an electrical field at the membrane – solution interface, a consequence of the second Wien effect, increases the degree of dissociation of weakly ionizable organic substances, which also promotes fouling of membranes.

The most widespread methods of prevention of a poisoning of membranes are the pretreatment of solutions and periodical polarity reversing. The most recent method of protection is to depositing on membranes surface a thin film with the same charge as the fouling substances. The charge density in the modifying film should be much less than the charge density of the membrane [5, 17].

6.3.2 Electrodeionization

Electrodeionization (EDI) is a process widely employed in chemical industry for ultrapure solution preparation. EDI is a membrane-based process driven by electrical current. The EDI process resembles ED. However the EDI stack has ion exchange material added to the desalination compartments. The filler can be in form of granules or fibers [5]. The major advantages of EDI over ion exchange is consistent part-per-billion and part-per-trillion level of contaminants; continuous high recovery operation; no chemical consumption for regeneration; no chemical waste; safety and reliability. The feed water requires pretreatment before entering the EDI process in order to meet requirements of low scaling potential and low level of fouling organic and colloidal particles. Commonly reverse osmotic permeates serve as a feed stream for EDI.

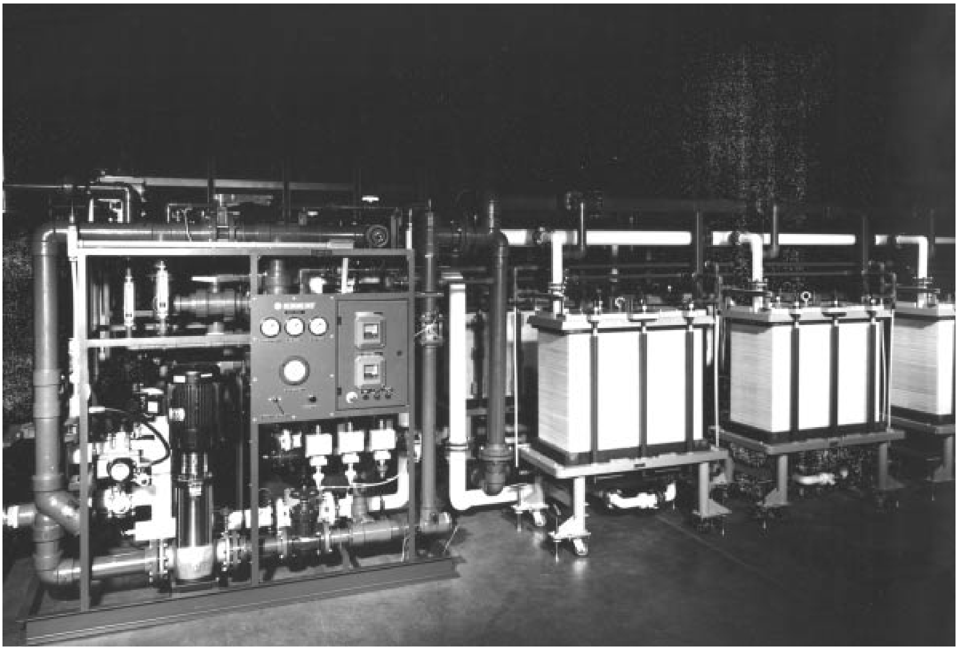


Fig. 6.5: General view of a commercial EDI installation produced by Ionics Inc.

In some instances, water produced by EDI with 10–18 megohm-cm resistivity can be used directly. Commonly EDI system is followed by mixed bed polishing filter in order to assure high purity. For customers EDI demineralization mean lower water treatment cost and less risk to downstream equipment and products.

The EDI stack consists of alternating pairs of strong cation and anion membranes, high quality ion exchange resins, polymeric flow channel spacers and a pair of electrodes. Electric current passing through the stack not only removes the ion present in the solution, but also splits water into hydrogen and hydroxide ions. These ions are continuously produced at points of contact between anion and cation exchange surfaces in the EDI stack (see 6.2.8). Constant flow of hydrogen and hydroxyl ions regenerates ion exchange granules and membranes inside the diluting compartment. Therefore there are favorable conditions for adsorption of weakly ionized substances. EDI has gained its popularity for very high removal rates of silica, carbon dioxide, and boron [18].

In order to avoid secondary contamination at the C→A contacts, the number of this contacts should be minimized by using uniform size beads in desalination compartment. Or the beads can be arranged in form of alternating layers where each layer contains only one type of ion exchange resin.

6.3.3 Electrochemical regeneration of ion exchange resin

Electrochemical regeneration of ion exchange resin is a process of electromigration by which previously absorbed counter ions are replaced by hydrogen and hydroxyl ions. The hydrogen and hydroxyl ions are generated either by bipolar membrane or on electrodes separated from resin by ion exchange membranes. The advantage of electrochemical regeneration over conventional chemical regeneration of ion exchange resin is reduction in chemical consumption and wastewater generation.

The kinetic study of this process reveals that in case of individual resin two different situation occur. The first situation takes place when the solution convection levels the concentration in all points, and the second one happens when there is no convection in the system.

If electric current is passing through ion exchange granules only, the degree of their regeneration (ω, fraction) can be characterized by the following equation derived from Faraday's law and mass balance [7]:

$$\eta Q = \frac{1}{\beta}\left(\ln\frac{1}{1-\omega} - \omega\right) + \omega$$

β the ratio of the ion mobility for ions coming in over the ions coming out.

$$Q = i\tau / F q_o$$

τ – time of current flow
q_o – ion exchange resin quantity
η – fraction of current carried by counter ions on the discharge side of the membrane

If there is no ion exchange between the different points of the system, then the ion exchange column regeneration can be described by the equation in following form:

$$\omega = \begin{cases} Q & Q \le \beta \\ \dfrac{2\sqrt{1-Q} - \beta(1+Q)}{1-\beta} & \beta \le Q \le 1/\beta \\ 1 & 1/\beta \le Q \end{cases}$$

It is necessary to use conductivity values determined at iso-electroconductivity conditions. Because the value β characterizes the ratio of ion mobility in an ion exchange resin or more precisely – in its gel portion. Analysis of the equations above shows that the rate of electrochemical regeneration should be higher if there is no ion exchange between different parts of the system. The source of ions for regeneration makes no difference for the regeneration rate.

Research on influence such as the fixed ion type, temperature, nature and concentration of a solution on kinetic and energy characteristics of process of electrochemical regeneration is reported [7]. The analysis of the reported equations shows that there is an optimum concentration of a solution at which the electric power consumption on regeneration is minimal. For sulfo-styrene cation exchange resin this minimum is about 0.01 to 0.03 eq/l. The power consumption would be 0.36, 0.95, and 2.3 kWh/eq for 30, 60, and 85 % regeneration accordingly.

Electrochemical regeneration of the mixed bed ion exchange resin can take place in both desalination and concentration chambers of electrodialysis apparatus. Withdrawal of ions from desalination chambers would be responsible for the resin regeneration in this chamber. Ions desorption on the C→A contact points and water splitting on the A→C contact points would carry out the regeneration in concentration compartment. In all cases current efficiency will increase as the current density grows.

6.3.4 Synthesis of new substances without electrode reaction participation. Bipolar membranes applications

The unique ability of ion exchange membrane to conduct ions selectively is a foundation for technological processes based on swapping ion mechanism. Double exchange

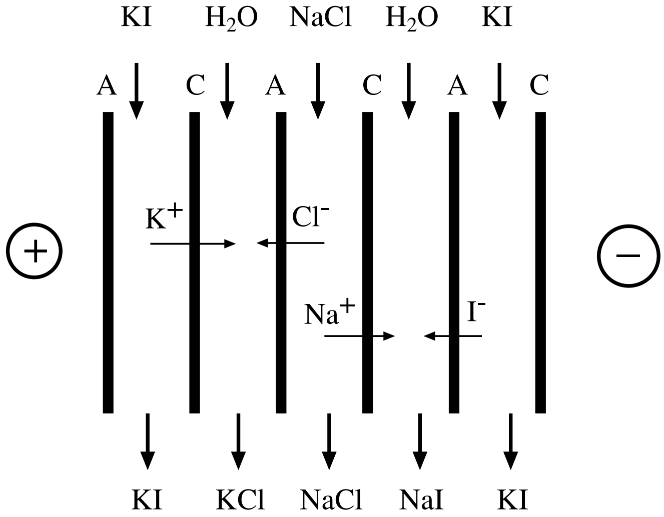


Fig. 6.6: Sketch of electrodialysis stack for double ion exchange reaction.

reaction by usual chemical methods is rather difficult, but it can be done easily with high efficiency in one stage in electrodialyser shown on the Fig. 6.6.

A bipolar membrane in an electric field generates hydrogen ion on one side and hydroxyl ion on the other side. Therefore electrodialysis with bipolar membrane can be used to produce acid and base from salt. For splitting 0.1 N NaCl at current density i = 20–150 A/m^2 concentrations of NaOH and HCl (C_{NaOH}, C_{HCl}, equiv./l) may be expressed as:

$$C_{NaOH} = 1.46 + 0.16\ i$$

$$C_{HCl} = 0.67 + 0.20\ i$$

Power consumption for generation of NaOH and HCl is 77.5…108 and 172…303 W^{-h} per equivalent at current density i = 40…100 A/m^2 [19].

This method would not require hazardous raw materials. For example the electrodialysers with bipolar membranes are applied for processing of spent solutions of HNO_3 and HF after stainless steel pickling. The solution is neutralized by KOH followed by removal of heavy metal hydroxide precipitates. Then KNO_3 + KF solution is treated in the electrodialysers with bipolar membranes. The solutions HNO_3 + HF and KOH are recovered and the cycle is repeated [20]. Bipolar membranes are used also for cation and anion-exchanger regeneration [21]. Bipolar membranes application in biochemical reactors allow very soft pH regulation without large pH change in the place of acid and alkali introduction [22], recycling of dimethyl isopropyl amines from a waste air stream, itaconic acid and sodium methoxide production [23]. A major commercial application is the conversion of organic acids and amino acids from their salts to the protonated form.

Bipolar membranes may be used to avoid the acid rain problem [24]. From 65 % to 90 % of the acid rain problem is due to sulfur dioxide pollution by smoke of power station. A process was developed to sorb sulfur dioxide from flue gases by sodium sulfite solution. Sodium sulfite was converted to sodium bisulfite [25]. Then in bipolar electrodialysers sodium bisulfite is converted back to sodium sulfite and pure sulfur dioxide (Fig. 6.7). Sodium sulfite is used for sulfur dioxide sorption again and pure sulfur dioxide may be used for sulfuric acid production. This process was demonstrated on a pilot scale in power plants in North America.

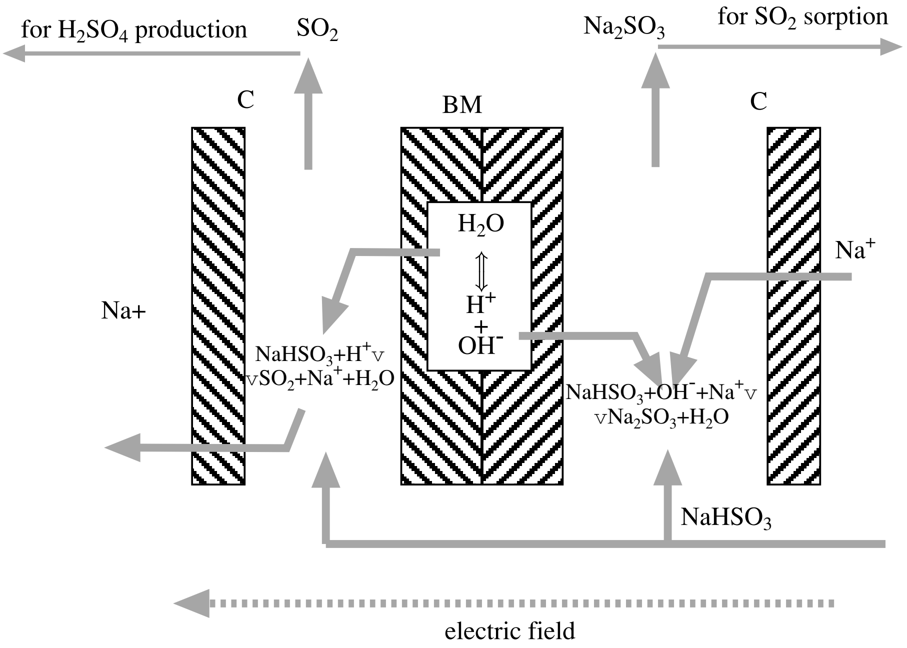


Fig. 6.7: Sodium bisulfite to sodium sulfite conversion by bipolar electrodialysis.

6.3.5 Isolation of chemical substances from dilute solutions

Ion exchange membrane may be used in a process aimed on isolation of a valuable chemical substance from dilute solutions. For example a dye can be extracted from a dilute solution [6]. The process is based on the reversible precipitation of the chemical compound on the surface of polarized ion exchange membrane. Electromembrane apparatus with the only one type of ion exchange membrane (anion – for anion dyes and cation – for cation dyes) are used for these prepossess. The ions are delivered to the membrane by diffusion and electromigration. Because membrane is not permeable for large dye molecules the concentration of dye increases near the membrane surface and reaches limit of its solubility. Then dye crystallization occurs and micro crystals get induced dipole moment. The first crystal layer is held by electrostatic interaction. The second and following layers are held by dipole-dipole interaction. After electric current is turned off dipole-dipole interaction disappears, the precipitate is re-suspended and it can been removed with a small volume of water. This method allows not only dye concentration but also dye purification from substances non-perceptible on membrane (for example well soluble non-organic and organic compounds) occurs. The following parameters of the process are described: flow velocity 0.6 cm/sec, C.I. Direct Black 3 concentration – 29 mg/l energy consumption 0.6–0.9 kWh/g for complete dye extraction, current density 50–100 mA/sq. cm, and capacity 430 mg/sq. m membrane surface. Dye concentration after desorption was 1–2 g/l. The highest degree of purity is confirmed by the fact that actual specific conductivity of dye produced is only a fraction of that reported in literature. Purification of colloids and ionized substances non-permeable for ion-exchanger membrane may be done using this method.

6.3.6 Electrodialysis applications for chemical solution desalination

Desalination of aqueous solution of valuable chemical products is an effective technology for purification of products recovered from waste streams in the chemical industry.

Of special note is the electrodialysis application for solution desalination in organic synthesis. For example electrodialysis with ion exchange membranes based on polystyrene and polyethylene for HCl removing from solution in chlorhydrin synthesis is reported [6]. It is possible to get 1N HCl from 1–3.5 g/l solutions with current efficiency 60 %. Transport coefficients for chlorhydrin derivatives do not exceeds 10–7 cm^2/s.

Desalination of 70–75 % diethyleneglycol solution by electrodialysis requires only 0.7–1.3 kWh/kg [6].

High water consumption by chemical industry makes very important usage of electrodialysis for wastewater recovery [26]. For example electrodialysis reversal demonstrated a stable performance and good fouling resistance in desalting wastewater from a paper mill [27]. The estimated cost of EDR treatment with 70 % TDS removal and 85 % recovery rate is \$8.52 / m^3.

6.4 Electrochemical processing with membranes

6.4.1 Electrochemistry

Electrochemical processing is a major part of the chemical industry. Primarily electrochemistry is used to achieve oxidation or reduction of chemicals. These redox reactions are achieved by using electrodes to add (or remove) electrons to a reactant. The reactant to be oxidized or reduced can be a gas, liquid, solid or solute, and often the redox reaction converts the reactant from one state to another. For example Cl^- ions in solution are oxidized to gaseous Cl_2 in a chlor-alkali cell, gaseous H_2 and O_2 are combined to produce electrical energy and liquid H_2O in a fuel cell, and metallic copper from an anode is converted to Cu^+ ion in solution.

Electrochemistry accounts for about 12 % of product value in the chemical and primary metal industries. Aluminum and magnesium are major contributors. Why are they produced electrolytically? It might be better to ask what other process would allow the production of such reactive metals. Indeed, the reason for using electrochemistry for a specific chemical transformation is probably because there are problems in achieving that transformation by more conventional means. Those problems might include unwanted side reactions or subsequent purifications to make an acceptable product. Electrochemistry requires the input of electrical energy, which is considerably more expensive than thermal energy. The efficiency of converting fossil fuel energy to electrical energy is only about 30 %. If the energy of the fossil fuel could be used directly to produce the material in the desired form and purity, electrochemistry would probably receive no consideration.

The benefit of using a membrane in an electrolytic cell can be illustrated in the electrolysis of NaCl. If an aqueous solution of NaCl flows between two electrodes, NaOH forms at the cathode, and Cl^- ions are oxidized to Cl_2 at the anode by the reaction

$$2Cl^- - 2e^- \rightarrow Cl_2 \qquad (1)$$

In an undivided electrolytic cell these two products will react quickly to form NaOCl. However, if an ion-permeable barrier is positioned between the electrodes, the gaseous Cl_2 and the NaOH can be recovered separately. The ion-permeable barrier in the divided cell can be made of a variety of materials. Prior to development of ion-exchange membranes, the barrier was an asbestos diaphragm. Modern chlor-alkali cells utilize perfluorinated sulfonic acid membranes based on poly(tetrafluoroethylene) (PTFE) which is commonly known as Teflon. DuPont developed the first commercial perfluorinated membrane and called it Nafion® [28]. Nafion, has been improved over the years and is the most commonly used membrane in divided electrolytic cells.

In contrast to the electrodialysis stacks discussed elsewhere in this chapter, the cells for electrochemical processing typically have one membrane, or at most a few membranes, between a pair of electrodes. A simple membrane cell is illustrated in Fig. 6.8. The components from left to right are anode, anode compartment containing the ano-

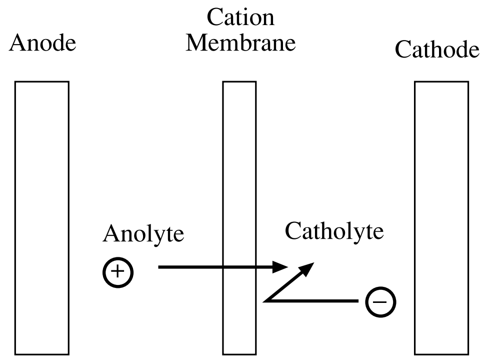


Fig. 6.8: Simple membrane cell for electrolysis.

lyte solution, cation-exchange membrane, cathode compartment containing the catholyte solution, and cathode. In a typical cell the electrodes are metal plates, but they can also be in the form of screens, fabrics, felts, porous sheets, or carbon blocks. The materials of the electrodes are varied to meet the needs of a particular situation. Except in cases where the electrode material is intentionally sacrificial, the electrode surface contacting the solution must be inert to avoid deterioration. Often the electrode surface is chosen to be catalytic in order to enhance the rate of a desired reaction and suppress an undesired reaction. When the electrode reactions are sufficiently selective, high product yields and substantial savings in product purification can accrue.

In some applications the electrolysis of water is the primary electrode reaction. That is the case at the cathode in a chlor-alkali cell.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

When NaCl is fed to the anode compartment, Na+ ions carry electric charge through the membrane. However, the membrane is not perfectly selective, and some OH- ions leak through into the anolyte. A small amount of HCl is added to the anolyte to neutralize the OH^- ions that leak through to avoid formation of $HClO^-$.

If the anolyte does not contain Cl^- or some other anion that is subject to oxidation at the anode, then O_2 will be generated at the anode by the reaction

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad (3)$$

Thus the electrolysis of water produces one mole of OH^- ion, one mole of H^+ ion, one-half mole of H_2, and one-quarter mole of O_2. In a 2-compartment cell the H^+ ions would carry electric charge through the cation-exchange membrane and neutralize the OH^- ions in the catholyte. Figure 6.9 shows a 2-compartment cell used to generate NaOH from Na_2SO_4. As long as the H^+ ions generated at the anode are consumed by the conversion of sulfate to bisulfate, current efficiencies are high and NaOH concentrations

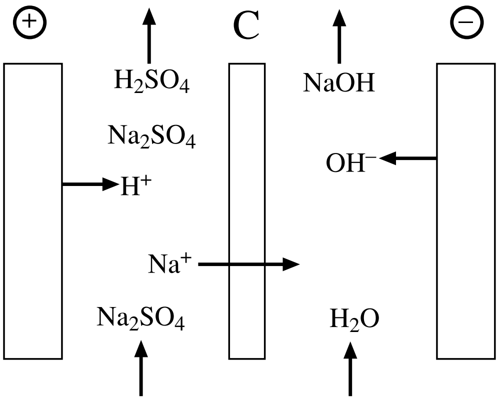


Fig. 6.9: Splitting Na_2SO_4 in 2-compartment cell.

up to 15 % are achievable. But Fig. 6.10 [29] shows the rapid decline in current efficiency as the H_2SO_4 concentration of the anolyte increases in a 2-compartment cell. Current efficiency can be substantially increased if a 3-compartment cell is used.

Figure 6.11 shows a 3-compartment cell with an anion-exchange membrane next to the anode and a cation-exchange membrane next to the cathode. A solution of Na_2SO_4 is flowing between the two membranes. H_2SO_4 is formed in the anode compartment by the transport of SO_4^{2-} through the anion-exchange membrane and the generation of H^+ ions at the anode. NaOH is formed in the cathode compartment just as in the chlor-alkali cell. Although the anion-exchange membrane does eliminate the Na^+ in the H_2SO_4 produced by this process, there is still some loss in current efficiency due to back-migration of protons through the anion-exchange membrane. One successful approach to eli-

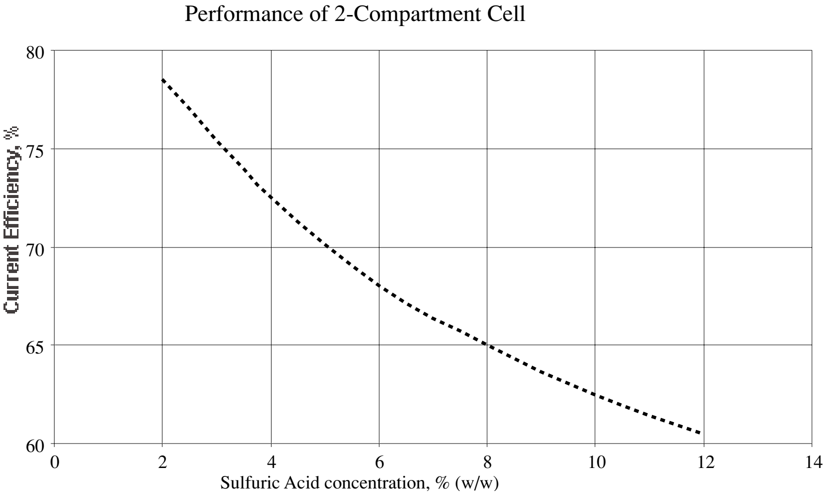


Fig. 6.10: Current efficiency as afunction of sulfonic acid concentration in a 2-compartment cell.

minating the loss in current efficiency was to inject ammonia into the anolyte [30]. Ammonia neutralizes the acid in the anolyte, and the $(NH_4)_2SO_4$ produced in the process is use as fertilizer. High-quality NaOH is still produced in the catholyte.

The 3-compartment cell shown in Fig. 6.11 has the limitation that the anion-exchange membrane is vulnerable to attack by the oxidizing conditions of the anode. There have been several variations of the 3-compartment cell that deal with this problem. The HYDRINA® process developed by De Nora overcame the problem by introducing H_2 gas at the anode as shown in Fig. 6.12 to eliminate the oxidizing conditions at the anode [31]. In fact, the H2 gas generated at the cathode can be used as the reducing gas at the anode. An added benefit is a lower cell voltage. Another approach to dealing with the anion-exchange membrane in the 3-compartment cell was to replace it with a perfluorinated cation-exchange membrane. In Fig. 6.13 the Na_2SO_4 solution is again fed to the center compartment where it is converted to $NaHSO_4$ by H^+ ions from the anode compartment. The solution then moves to the anode compartment where more of the Na^+ ions are replaced with H^+ ions to form H_2SO_4. But the conversion is not complete because the more mobile H^+ ions begin to carry more of the current as their relative concentrations builds up.

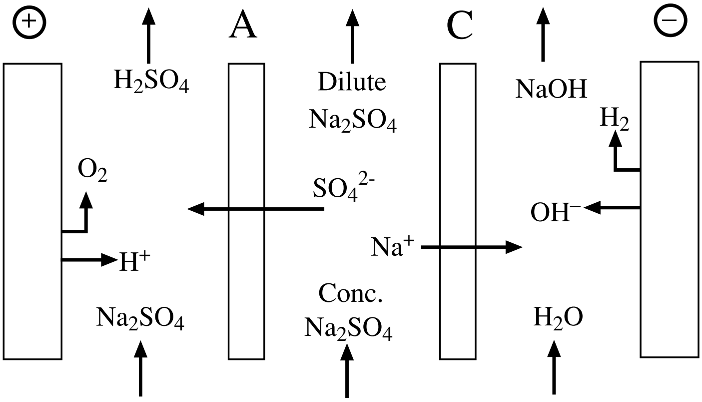


Fig. 6.11: Splitting Na_2SO_4 in 3-compartment cell.

The 3-compartment cell is satisfactory for acids that do not decompose at the anode, but it would be unsatisfactory for splitting NaCl, because Cl_2 would form at the anode. To alleviate that problem a cation-exchange membrane could be added next to the anode, and H_2SO_4 could be circulated as the anolyte. The additional membrane could be a perfluorinated membrane that resists oxidation at the anode, and that addition would improve the chemical stability of the cell.

The reader might reasonably want to compare at this point the relative merits of splitting a salt by electrolysis or with bipolar membranes discussed elsewhere in this chapter. Electrolysis has the advantages that the acid and base can be made more pure, at

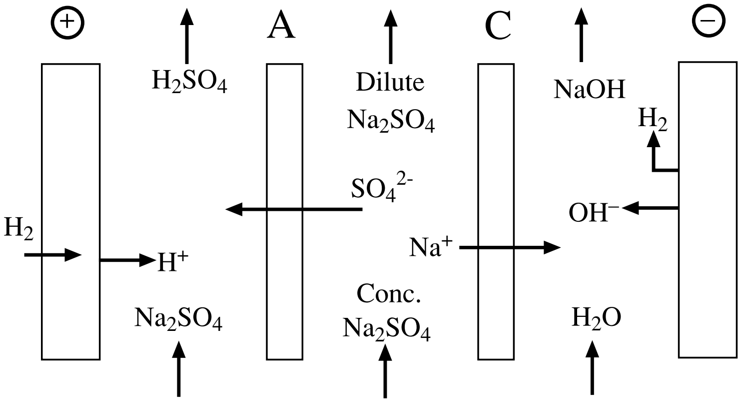


Fig. 6.12: HYDRINA® process for splitting Na_2SO_4.

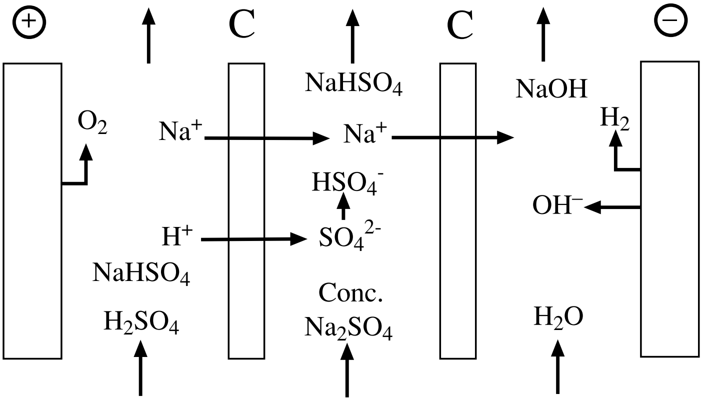


Fig. 6.13: Splitting Na_2SO_4 with two cation membranes.

higher concentrations and with higher operating current density. Bipolar membranes have the advantage of substantially lower energy consumption and probably lower capital cost.

6.4.2 Chlor-alkali industry

Production of Cl_2 and NaOH by electrolysis of NaCl is a huge industry with annual production capacity in excess of 50 million tons of NaOH per year. Membrane cells are the state-of-the-art technology, but mercury and diaphragm cells are still used because the capital cost for their replacement is substantial. The mercury cell technology is more than a century old and still accounts for nearly half of the world's production capacity.

Chlorine evolves from a DSA (dimensionally stable anode) situated above a pool of mercury with NaCl brine in between. Mercury reacts with sodium to form sodium amalgam, which is removed and hydrolyzed in a separate reactor.

$$Na^+ + Hg + e^- \rightarrow NaHg \quad 2NaHg + 2H_2O \rightarrow H_2 + 2NaOH + 2Hg \tag{4}$$

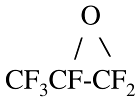
The reconstituted metallic mercury is returned to the cell. The major advantage to the mercury cell is that it produces very pure NaOH at 50 % concentration. But electrical energy consumption is high, and the threat of mercury pollution is a major concern. Traces of mercury appear in the NaOH and in air emissions from the cells. Because of their design it is impractical to modify mercury cells into membrane cells.

The diaphragm cell has a membrane of sorts, with a sheet of asbestos felt separating the two compartments. The diaphragm keeps the chlorine gas out of the cathode compartment, but it offers no selectivity for diffusion and migration of ions. Therefore, the NaOH produced is dilute (12 % maximum) and loaded with NaCl. Evaporation of the catholyte to concentrate the NaOH to 50 % causes most of the NaCl to precipitate, but the chloride level of the product remains about 1 %. In some cases the asbestos diaphragms have been replaced with other porous membranes (principally PVC) to improve membrane life and avoid environmental criticism. In other cases diaphragm cells have been converted to membrane cells.

Membrane cells are acknowledged as the most efficient for chlor-alkali. Since the process is so energy-intensive and the market is so large, there has been considerable competition to improve membranes, electrodes, cell design and operating conditions. Moreover, the technology developed for the chlor-alkali industry has been beneficial to the electro-membrane processing in general. Therefore, it would be useful to describe some of the technology developments here.

6.4.3 Perfluorinated membranes

The development of perfluorinated membranes has been most important to the progress in membrane cells. The first perfluorinated membranes were made by DuPont, and they were followed by products from Asahi Glass [32] and Asahi Chemical in Japan where membrane cells are now dominant. Because of their Teflon®-like chemical composition, perfluorinated membranes resist chemical and thermal degradation better than any of the hydrocarbon ion-exchange membranes that preceded them. For most of them the starting materials are perfluorinated monomers such as tetrafluoroethylene (TFE) $CF_2{=}CF_2$ and hexafluoropropylene oxide (HFPO)



$$\overset{O}{\overset{/\ \backslash}{CF_3CF\text{-}CF_2}}$$

The preparation of perfluorinated membranes from these monomers is rather complex, and several research groups developed different routes to similar end points. Typically they utilized the monomers TFE and HFPO and a variety of other reagents to synthesize a complex perfluorinated monomer (PFM) containing ether linkages. The general structure of PFM is

$CF_2{=}CF\text{-}(OCF_2\text{-}CFCF_3)_p\text{-}O\text{-}(CF_2)_q\text{-}X$ $X{=}SO_3^-$ or COO^-; $p{=}0\text{-}2$; $q{=}1\text{-}4$

The TFE and PFM monomers are then copolymerized by radical-initiated polymerization to make a polymer of the structure

$[(CF_2\text{-}CF_2)_m\text{-}CF_2\text{-}CF\text{-}(OCF_2\text{-}CFCF_3)_p\text{-}O\text{-}(CF_2)_q\text{-}X]_n$ $m{=}6\text{-}8$; $n{=}600\text{-}1500$

Calculation of the formula weight for n=1 gives the "equivalent weight" for the polymer, which is the average polymer weight per ionic charge. (Membranes with higher equivalent weight have higher permselectivity but also higher electrical resistance.) For DuPont's Nafion R1100 resin used to make most of its membranes, the values of variables in its PFM are p=1, q=2. Knowing that the equivalent weight is 1100 allows one to calculate a value of m=6.56. This indicates that well over half of the membrane is comprised of a Teflon®-like structure.

Before fabrication of the membranes, the terminal group is converted to a more stable form, sulfonyl fluoride or methyl carboxylate. Then the copolymer is extruded to form a membrane. The extruded films can be further processed to achieve a variety of membrane properties. They can be laminated with PTFE fabric to produce a reinforced membrane, and membranes made of polymers with different values of m, n, p or q can be laminated to form composite membranes with desired properties. After fabrication is complete, the X group is restored by hydrolysis.

Perfluorinated membranes used in chlor-alkali cells normally have a thin layer of carboxylate on the cathode-facing surface of a sulfonate membrane. Nafion 901 was introduced as such a membrane [33]. It achieved 33 % NaOH production with 95 % current efficiency in cells operating at 3 kA/m^2 and 3.3 to 3.9 V. The carboxylate layer can be prepared by lamination, but the layer can be thinner if it is made by surface treatment. That modification is made by treating a surface of the sulfonate membrane successively with phosphorus pentachloride, hydrazine and mild oxidation. The carboxylic acid layer on the membrane is beneficial because it helps in the rejection of hydroxyl ions, the transport of which reduces the current efficiency of the process. Sulfonate membranes tend to be leaky to bases, and any base that leaks through to the anolyte must be neutralized by addition of HCl to the brine so that its pH can be maintained between 2 and 4. A higher pH promotes NaOCl and O_2 formation. A lower pH reduces current efficiency, because H^+ ions compete with Na^+ ions in transporting current through the membrane. If H^+ ions reach the carboxylate layer of the membrane and convert it to the carboxylic acid, the membrane resistance increases dramatically.

6.4.4 Process conditions

With the carboxylate layer on the membrane, the concentration of NaOH in the catholyte can be maintained at about 32 %, which compares favorably with the 12 % product from diaphragm cells. Consequently considerably less thermal energy is needed for evaporation to the commercial 50 % product.

Voltage requirements vary inversely with temperature, so it is advantageous to operate at elevated temperatures. The perfluorinated membranes can tolerate sustained temperatures of 90ºC.

Because the anolyte and catholyte are both quite concentrated, there are osmotic forces at work to dehydrate the membrane. To some extent dehydration is beneficial, because it increases the ratio of sulfonate to water in the membrane, which in turn improves permselectivity. But eventually the dehydration leads to an increase in membrane resistance. Therefore, raising the NaOH concentration to reduce evaporation costs would likely increase electrical power costs.

Calcium and magnesium in the brines can cause major problems in chlor-alkali cells, because these ions will migrate through the membrane along with the Na+ ions. But the pH gradient across the membrane prevents the completion of their passage due to the insolubility of their hydroxides. Build-up of $Ca(OH)_2$ and $Mg(OH)_2$ causes an increase in membrane resistance, and even worse, disruption of the membrane structure. To avoid these problems, calcium and magnesium must be removed from the brine before it is introduced to the electrolytic cell. Chelating ion-exchange resins in the Na+-ionic form are typically used to remove these ions to concentrations of a few parts per billion.

Electrode materials in chlor-alkali cells are typically nickel for the cathode and RuO_2-coated titanium for the anode. The composition of the coating can have a dramatic effect on the cell voltage. The RuO_2 coating protects the titanium from oxidation and catalyzes the preferred gas evolution reaction to generate Cl_2. Some chlor-alkali cells have noble-metal coating on the nickel cathode to reduce cell voltage.

6.4.5 Zero-gap electrode configurations

In the diagrams of electrolytic cells shown above to illustrate the electrode and membrane configurations, the anolyte and catholyte are shown to flow between the membrane and the electrode surface. The gap between the membrane and the electrode allows space for the gas bubbles to disengage and allows for flow of solution delivering the ions such as Cl^- to the electrode surface. However, the gap is not always necessary. Often the molecules that react at the electrode surface are the solvent, typically water dissociating to form H^+ and O_2 or OH^- and H_2. In such cases the solvent is already present at the electrode surface. But there is still a need to remove the gas so that it does not block the flow of electric current between the electrode and the membrane. In "zero-gap" configurations, the gas is allowed to escape through the electrode. This can be done by utilizing a screen, grid or perforated metal electrode or by making the electrode porous. In some cases the membrane is held firmly against the electrode by applying a pressure differential across the membrane. In other cases the membrane is formed directly on the surface of the porous electrode.

The zero-gap design is also utilized for processes in which gases are consumed at the electrodes. The most noteworthy example is in fuel cells where H_2 and O_2 react at the electrode surfaces to form H_2O and release electrical energy.

Porous electrodes must be carefully designed to ensure that four processes can occur:

- gas transport to or from the electrode surface
- flow of electrons via a continuous path of electrode material
- transport of ions to and through the membrane material
- transport of solvent to the reaction site (except in fuel cells)

Ideally four media, a hydrophobic pore connected to a gas manifold, a protrusion of the electrode, a protrusion of the membrane, and a hydrophilic pore connected to a solvent manifold, would converge at a point that is geometrically optimized so that the resistance to transfer is the same in all four media. Further there would need to be an abundance of these convergence points packed into a small volume with very short transport distances to minimize resistances. Practically it is very difficult to achieve the convergence of four separate media and maintain their connectivity with short transport distances. Therefore, it is usually necessary for one or more of the media to perform double or triple duty.

In the conventional design where a solution flows between the membrane and the electrode surface, the solution must perform three of the functions listed above. That solution must contain an electrolyte so that ions can transport the current through the gap. The formation and growth of gas bubbles blocks the current flow, so the bubbles must be swept away by swift solution flow.

In Zero-gap membrane-electrode assemblies the membrane performs the double duty of ion removal and delivery of solvent molecules to the electrode surface. Since the water flux is proportional to the membrane thickness, it is desirable to have very thin membranes, which is much easier when the membrane and electrode are manufactured as one piece.

By their very nature porous zero-gap systems are three-dimensional. They are comprised of interpenetrating media for conduction of electrons, ions, solvent and gas. Often they are made as composites of fibers, powder, polymers, metals, etc, that are mixed, pressed and cured to form felt-like structures.

6.4.6 Other electrolytic processes

As mentioned above, the electrolysis of NaCl to from Cl_2 and NaOH is the largest application of membranes in electrolytic cells. There are also other brine electrolyses of commercial importance. NaBr brine is electrolyzed to form Br_2. (Another method of Br_2 formation is to treat bromide brines with Cl_2 derived from electrolysis.) Electrolysis of KCl brines is the preferred process for making KOH. Because K^+ ions are less hydrated than Na^+ ions, the membrane is more effective at blocking the back diffusion of KOH, which allows production of KOH in concentrations as high as 47 %.

Chlorine is used on a large scale for production of chlorinated hydrocarbons with vinyl chloride monomer being the largest single product. Until recently Cl_2 had been a mainstay oxidizing agent for many industries, the two major applications being disinfection of drinking water and bleaching of the brown fibers from wood to produce white paper. Then pressure from environmentalists forced the industry to seek oxidizing agents that were perceived to be more acceptable. The major objection to Cl_2 seems to be the unwanted chlorinated byproducts that result from reactions with organics. Chlorine dioxide ClO_2 overcomes that objection, but it has the disadvantage that it cannot be stored and shipped safely. Instead, it must be produced on site from another oxidizing agent, sodium chlorite, $NaClO_2$. Some chemical routes to this conversion are

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad (5)$$

$$2NaClO_2 + NaOCl + H_2SO_4 \rightarrow 2ClO_2 + NaCl + Na_2SO_4 + H_2O \qquad (6)$$

which have the unwanted byproducts NaCl and Na_2SO_4. An electrochemical alternative is to convert $NaClO_2$ to ClO_2 at the anode by the reaction

$$2NaClO_2 \rightarrow 2ClO_2 + Na+ + 2e^- \qquad (7)$$

This process has the advantage of no unwanted byproducts. Moreover, the yield of ClO_2 can exceed 90 %.

Another precursor for ClO_2 is sodium chlorate $NaClO_3$. The pulp and paper industry consumes 95 % of global chlorate production. The $NaClO_3$ can be reduced to ClO_2 by several different agents, which are listed below along with their reactions:

$$SO_2 + H_2SO_4 + 2NaClO_3 \rightarrow 2ClO_2 + 2NaHSO_4 \qquad (8)$$

$$2HCl + 2NaClO_3 \rightarrow 2ClO_2 + NaCl + 0.5\ Cl_2 + H_2O \qquad (9)$$

$$2CH_3OH + 6H_2SO_4 + 9NaClO_3 \rightarrow 9ClO_2 + 3Na_3H(SO_4)_2 + 0.5CO_2$$

$$+ 1.5HCOOH + 7H_2O \qquad (10)$$

$$3H_2O_2 + 4H_2SO_4 + 6NaClO_3 \rightarrow 6ClO_2 + 2Na_3H(SO_4)_2 + 6H_2O + 3O_2 \qquad (11)$$

All of these reactions produce some unwanted byproducts, which can be avoided by splitting $NaClO_3$ in a 3-compartment cell to chloric acid, $HClO_3$, which can be stored and shipped safely [34]. The $NaClO_3$ is fed between two cation-exchange membranes, and H^+ ions from the anolyte replace Na^+ ions that migrate to the catholyte to form NaOH co-product. The $HClO_3$ can be catalytically converted to ClO_2 by the reaction

$$4HClO_3 \rightarrow 4ClO_2 + 2H_2O + O_2 \qquad (12)$$

Chloric acid is also produced directly from HOCl in the anode compartment of a 2-compartment electrolytic cell [35].

$$4HOCl + 2H_2O - 6e^- \rightarrow 2HClO_3 + Cl_2 + 6H^+ \qquad (13)$$

Sodium hydrosulfite, $Na_2S_2O_4$, also known as sodium dithionite, is a reducing agent used industrially in the processing of pulp and paper, textiles and clay. It is made in a 2-compartment cell with a nickel anode and a special flow-through cathode made of stainless-steel fibers [36]. The starting material is SO_2 that reacts with water to form H_2SO_3. The reduction takes place in the cathode compartment.

$$2H_2SO_3 + 2e^- \rightarrow S_2O_4^{2-} + 2H_2O \qquad (14)$$

The reader has probably noticed by now that in many of the processes described the right-hand side of the cell has the same electrolytic reaction

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (15)$$

Indeed, with a few exceptions such as the production of $Na_2S_2O_4$, the majority of electrochemical processing seems to be oxidation at the anode and/or removal of a cation through a membrane. This means that electrochemical processes produce large volumes of H_2. In fact, some plants are designed to produce H_2 by electrolysis of water. In that process the anode reaction is

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad (16)$$

Thus a Faraday of electric charge produces 1/2 mole of H_2 and 1/4 mole of O_2, and the gases are very pure. The major criterion for keeping the gases pure is avoidance of mixing. This can be done in the laboratory by simply performing the electrolysis in a U-shaped tube containing H_2SO_4 with the electrodes positioned high enough so that the gases move upward to collection points, but this arrangement requires excessive energy to push the current through the large gap between the electrodes. A more energy-efficient apparatus utilizes a membrane to separate the electrodes, one of which can have zero-gap. With adequate supply of water to the electrodes, both can be zero-gap.

6.4.7 Fuel cells

Chemists usually consider a gas-producing reaction to be irreversible, because one of the reaction products, in this case the gas, is removed from the reaction site. But if the gas is retained at or introduced to the reaction site, the process can be reversible. H_2 and O_2 can be brought together and burned to form water and release energy, or they can combined in the reverse of the electrolysis reaction to form water and electrical energy. The apparatus for conversion of H_2 and O_2 to electrical energy is the fuel cell, and those containing ion-exchange membranes are often called PE (polymer electrolyte), PEM (proton exchange membrane) or SPE (solid polymer electrolyte) fuel cells. Of course there are several different types of fuel cells that do not utilize membranes, but they are outside the scope of this chapter.

Fuel cells can be used to recover energy from the H_2 gas generated by an electrolytic cell. Since both processes operate with direct current, the cost of rectifiers is avoided. Return on investment for a fuel cell in such an application is reported to be about 5 years. In some situations it might be advisable to consider reusing the H_2 directly in the electrolytic cell to depolarize the anode. Such schemes have been proposed for cells where O_2 is usually evolved at the anode [37]. Depolarization reduces the over voltage at the anode and allows about the same amount of energy recovery with just a modification to the existing electrolytic cells instead of the expenditure for fuel cells.

Figure 6.14 shows the structure and operation of the membrane fuel cell. The membrane is sandwiched between two porous electrodes coated with a thin layer of platinum catalyst. H_2 gas enters through the porous anode and reacts on the catalyst surface to form protons and release electrons. The electrons move through the external electrical circuit. The protons move through the membrane, which is impermeable to electrons and the gases. O_2 adsorbed on the cathode catalyst where it picks up electrons to form oxygen anions, which react with protons to form water. The fuel cell can produce up to 1 volt, but generally operates at 0.5 to 0.8 volts depending upon the current, and its energy efficiency approaches 50 %. Stacking individual fuel cells with their electrodes connected in series allows output voltages to be increased to practical levels. The main incentive for developing membrane fuel cells is the prospect that they can be used to power automobiles. A major drawback is the high cost of platinum catalyst and membranes, but these costs are coming down with designs improvements that require lower catalyst loadings and thinner membranes.

Perfluorinated membranes have the physical characteristics necessary for fabrication and operation in a fuel cell, but their cost is prohibitive. Alternative materials are being developed that could provide cheaper membranes that equal or even exceed the performance of Nafion. One example is membrane formed by grafting onto poly(vinylidine fluoride) (PVDF) film [38]. An 80 µm PVDF film is irradiated under nitrogen in

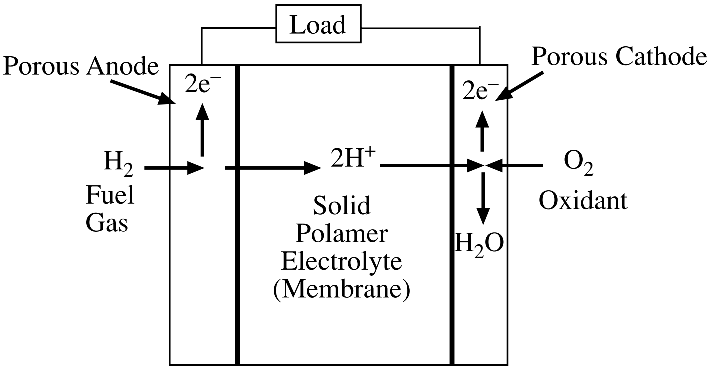


Fig. 6.14: Membrane or SPE fuel cell.

an electron accelerator and immediately soaked in a solution of 80 % styrene monomer and 20 % tetrahydrofuran under reflux at 70°C. The degree of grafting is determined by the time of contact (0.4 to 4 hr), and at least 20 % grafting is needed to ensure penetration to the center of the film. After chloroform extraction to remove unreacted monomer and ungrafted homopolymer, the film is treated with 0.5 M chlorosulfonic acid in 1,2-dichloroethane at ambient temperature for 24 hr to obtain 95 % sulfonation of the grafted polystyrene. The grafted PVDF membrane was reported to perform as well as Nafion in fuel cell tests.

Membrane fuel cells have zero-gap electrodes on both sides of the membrane. Typically the electrodes are made of a carbon fiber mat impregnated with platinum on carbon (Pt/C) catalyst. To achieve an extended surface for the gas to be adsorbed and react and to maintain continuity for ionic transport, interpenetration of electrode and membrane is necessary. This is usually accomplished by impregnating the porous electrode with Nafion solution. One assembly technique is to suspend the Pt/C in Nafion solution by sonication and spray it onto carbon paper. Then the membrane is hot pressed between the two impregnated electrodes [39]. Another approach is to make an aqueous suspension of three powders – Pt/C, carbon black, and PTFE – and spray it onto the carbon paper. Then 5 % Nafion solution is applied by spraying of by floating the electrode on the Nafion solution, after which the membrane is pressed between the electrodes [40]. The Nafion solution serves as an adhesive as well as a means of extending the electrolyte into the structure of the porous electrode.

Gore-Select membrane is a recent innovation that is useful for fuel cells. The membrane is made by filling the pores of Gore-Tex (expanded PTFE) with a perfluorinated ionomer like Nafion. The resulting membrane is about 20 μm thick, about one tenth the thickness of a Nafion membrane, and it has about half the resistance of Nafion. Membrane electrode assemblies are made by applying platinum black coatings (0.3 mg/cm^2) to both surfaces. They are reported to perform well in fuel cells [41].

6.4.8 Electroorganic synthesis

Many examples of electroorganic synthesis have been reported and a few are commercial. The first significant commercialization of electroorganic synthesis was the electrohydrodimerization (EHD) of acrylonitrile to adiponitrile, an intermediate for hexamethylenediamine, which is a monomer for nylon.

$$2CH_2 = CHCN + 2H_2O + 2e^- \rightarrow NC(CH_2)4CN + 2OH^- \qquad (17)$$

The reduction takes place at the cathode with a catholyte composed of aqueous quaternary ammonium salt. The anolyte is sulfuric acid. H^+ ions generated at the anode pass through the membrane and neutralize the OH- ions generated in the catholyte. Commercial installations are operated by Solutia (spun off from Monsanto), BASF, Asahi Chemical, and Rhodia. Some of these manufacturers have developed undivided cells for this process.

In some syntheses, including the EDH described above, the organic to be modified is brought directly into contact with the electrode. In other cases indirect electrosynthesis is accomplished with an intermediate redox agent such as cerium, which can have its oxidation state changed in an electrochemical cell. There are benefits to using an intermediate redox agent. An inorganic agent is typically more soluble in aqueous systems, and it can be treated at high current densities without unwanted side reactions. Since the electrochemistry can be separated from the chemical step, both processes can be optimized.

An example is the oxidation of naphthalene with cerium, which has been demonstrated on a pilot scale [42]. Ce(III) in and aqueous solution of methanesulfonic acid is oxidized to Ce(IV) at the anode. The Ce(IV) reacts with naphthalene in a separate vessel to form naphthoquinone and Ce(III). The aqueous phase containing the methanesulfonic acid and Ce(III) is separated and returned to the electrolytic cell. The naphthoquinone is an intermediate for dyes, agricultural chemicals, and anthraquinone, which is made by a Diels-Alder reaction with butadiene.

6.4.9 Electrochemical oxidation of organic wastes

Widely practiced disposal methods for organic wastes, incineration, biological degradation, and landfill are unacceptable for some wastes because of the presence of hazardous materials in the waste. A case in point is the accumulation of plutonium-contaminated tissue paper in a nuclear laboratory, which led to the development of an oxidation process called “Silver Bullet” based on Ag(II) generation at an anode [43]. A mixture of the organic waste and $AgNO_3$ is circulated through the anode compartment where Ag(I) is oxidized to Ag(II), which then reacts with the organic material to convert it to CO_2. Side reactions with water and nitrate form OH and NO_3 free radicals that also aid in the destruction of the organics. Heteroatoms are also oxidized, phosphorus to phosphate and sulfur to sulfate, and these must be removed by a bleed of the anolyte. Chloride is partially oxidized to chlorine gas, but some AgCl also forms. The process is effective on a variety of wastes including pesticides.

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7 Membrane Technology in the Chemical Industry: Future Directions

R. Baker

7.1 The past: basis for current membrane technology

Attempts to use membranes for practical separations did not begin until the early 1900s when Bechold, Zigmondy and Bachmann, and Elford and Ferry used nitrocellulose membranes to separate laboratory solutions by dialysis and microfiltration. By the 1930s microporous membranes were commercially produced on a small scale and, at about the same time, Teorell, Meyer, and Sievers made the first practical ion-exchange membranes and developed their theory of ion transport through charged membranes. As a result, the elements of modern membrane science were in place by the late 1960s, but essentially no industrial applications of membranes existed. The total membrane industry was probably less than U.S. $10 million/year (in current dollars). Membranes were used in a few laboratory and analytical applications, but not for industrial applications because they were too slow, too expensive, and too unselective. The development of solutions to these problems has led to the current widespread and growing use of membranes in the chemical and refinery industries.

7.1.1 Ultrathin membranes

The seminal discovery that transformed membrane separation from a laboratory to an industrial process was the development in the 1960s of the Loeb-Sourirajan process to make defect-free ultrathin cellulose acetate membranes [1]. Loeb and Sourirajan were trying to use membranes to desalt water by reverse osmosis (RO). The concept of using a membrane permeable to water and impermeable to salt to remove salt from water had been known for a long time, but the fluxes of all the membranes then available were far too low for a practical process. The Loeb Sourirajan breakthrough was the development of an anisotropic membrane. The membrane consisted of a thin, dense polymer skin 0.2- to 0.5-µm thick supported on a much thicker microporous layer. The thin, dense skin layer performed the separation; the microporous support provided the mechanical strength required. These membranes had 10 times the flux and equivalent selectivities to the best membranes then known. Once the advantages of the anisotropic structure had been demonstrated by Loeb and Sourirajan, many other ways of making anisotropic membranes were developed. Anisotropic membranes with effective thicknesses of 0.05 to 0.1 µm are now produced on a large scale.

7.1.2 Membrane modules

The second advance that made industrial membrane separation processes possible was the development of methods to incorporate large membrane areas into economical membrane packets or modules. Even with the best anisotropic membranes, most industrial processes require several hundred, sometimes several thousand, square meters of membrane to perform the separation. The three most important configurations, shown schematically in Fig. 7.1, are hollow-fine-fiber, capillary-fiber and spiral-wound modules. Tubular and plate-and-frame modules are also used, but their high cost limits them to small-scale or specialized applications. The advantages and disadvantages of the various module types are summarized in Tab. 7.1.

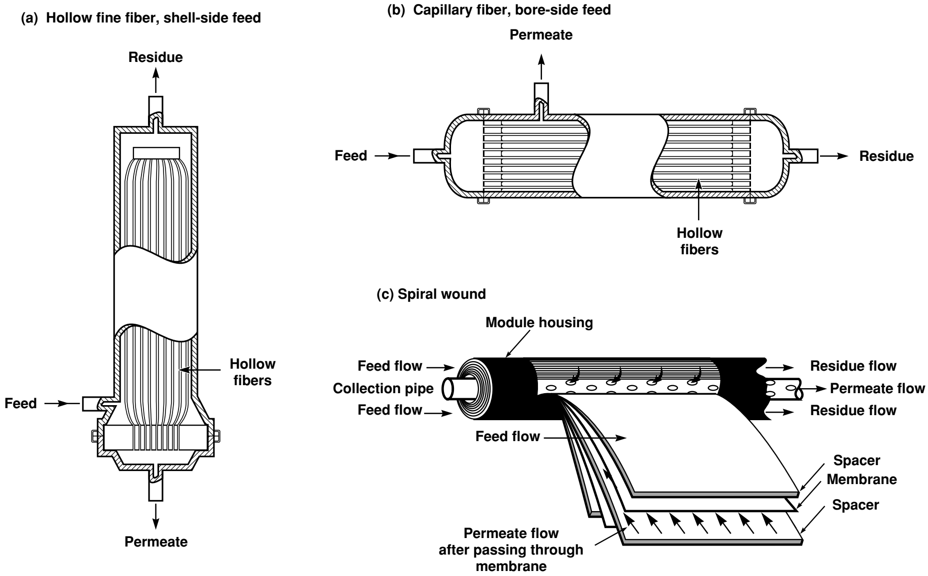


Fig. 7.1: Membrane module configurations.

Hollow-fine-fiber membranes are tiny polymeric tubes with diameters of 100 to 250 µm. Between 0.5 and 2 million fibers are packed into an average 20-cm-diameter module. This allows a very large membrane area to be contained in a relatively small volume. Because high speed automated equipment is used to spin the fibers and prepare the membrane modules, the production cost of these modules on a per square meter basis

Table 7.1: Membrane module characteristics.

Module Type	**Manufactoring Cost* (US$/m²)**	**Area of Standard Module** (m²)**	**Characteristics**
Hollow Fine Fiber	**2–10**	**300–600**	**Low cost per m² of membrane but modules easily fouled. Only suitable for clean fluids.**
Capillary Fiber	**5–50**	**50–150**	**Limited to low pressure applications <200psi; good fouling resitance, can be backflushed. Important in ultrafiltration (UF) and microfiltration (MF) appl.**
Spiral Wound	**10–50**	**20–40**	**The most common RO module. Increasingly used in UF and gas separation applications.**
Tubular Plate and Frame	**50–200**	**5–10**	**High cost limits applications.**

* Cost here is manufacturing cost, selling prices are typically two to five times higher.
** A standard module is defined as 20 cm (8 in) in diameter and 100 cm (40 in) long.

is low, in the range US$ 2–10/m². This cost is the module manufacturing cost; the selling price is higher and reflects the pricing structure adopted by that segment of the industry. Capillary-fiber modules are similar to fine-fiber modules but have larger diameters, generally in the range 500–2000 µm. In capillary fiber modules, the pressurized feed fluid passes down the bore of the fiber. In hollow-fine fiber modules, the pressurized feed fluid usually enters the shell side of the fibers, and the permeate fluid passes down the fiber bore.

The relatively low cost of hollow-fiber modules is their principal advantage. A key disadvantage is that the polymer membrane must perform the separation required as well as withstand the pressure driving force across the membrane. Preparing membranes that meet both requirements is difficult. Thus, producing membranes that have high selectivities and high fluxes and that are mechanically stable is far more difficult in hollow-fiber form than with the flat sheets used in spiral-wound modules. As a result membranes used in spiral-wound modules generally have better, sometimes significantly better, performance than their hollow fiber equivalents. In some cases the best membranes cannot be formed into hollow fibers. Because hollow-fiber membranes must support a relatively high pressure, softening of the microporous support by absorbed materials can lead to catastrophic failure. Plasticization and collapse of the microporous support layer can also be a problem with the flat-sheet membranes used in spiral-wound modules. However, in this case the pressure is supported by the microporous layer and a nonwoven paper support, so the membranes are generally more robust. A final issue with hollow-fiber modules, particularly fine-fiber modules, is their susceptibility to fouling by particulate matter carried into the module with the feed fluid.

For these reasons, despite their apparent cost advantage, hollow-fiber modules are generally limited to separations involving clean particulate-free feed fluids, for example, desalination of seawater, separation of nitrogen from air, and separation of hydrogen from nitrogen, methane and argon in ammonia reactor purge gas.

7.1.3 Membrane Selectivity

The third development of the last 40 years that has made membranes widely applicable to industrial separations is the availability of more selective, more permeable membrane materials. In the 1960s and 70s membranes were generally made from commercially available polymers developed for other purposes. More recently membrane developers are increasingly using tailor-made polymers. The result is a significant improvement in membrane properties for a number of separations. As an example, Fig. 7.2 shows a plot due to Robeson showing the permeability and oxygen/nitrogen selectivities of a large number of membrane materials [2]. There is a strong inverse relationship between flux and selectivity. This selectivity/permeability tradeoff is very apparent in Robeson's plot, which shows the data for a large number of polymers reported in the literature. Also shown in the figure is a line linking the most permeable polymers at a particular selectivity; this line is called the upper bound, beyond which no better material is currently known. The relative positions of the upper bound in 1991 and in 1980 shows the progress that has been made in tailor-making polymers for this separation. Development of improved membrane materials is a continuing topic of research, so further slow movement of the upper bound is likely.

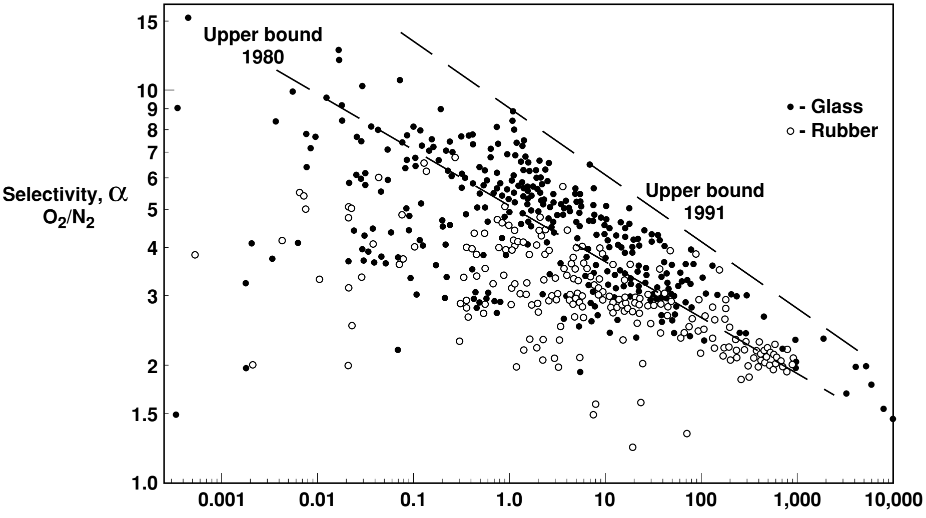


Fig. 7.2: Robeson's plot of membrane oxygen/nitrogen selectivity as a function of oxygen membrane permeability for all polymers known [2].

7.2 The present: current status of the membrane industry

7.2.1 Reverse osmosis

Reverse osmosis was the first membrane process to be used on a large commercial scale, following the development of the Loeb-Sourirajan membrane (1962) and the timely infusion of substantial research dollars by the U.S. Office of Saline Water. Membrane and module technology was sufficiently developed for commercial plants to be installed by the late 1960s. The development of interfacial polymerization as a technique to produce composite membranes by Cadotte was another major milestone; currently these membranes have about 80 % of the total reverse osmosis market [3]. Hollow-fine-fiber membranes, widely used in the 1970s and 80s, are increasingly being displaced by the more reliable spiral-wound modules. Currently approximately 1 billion gallons/day of water are desalted by reverse osmosis. About half of this capacity is installed in the Middle East and other desert regions to provide municipal drinking water. The remainder is used in the industrial world to produce ultrapure water for the electronic and pharmaceutical industries.

The reverse osmosis industry is now well established; three or four manufacturers produce 70 % of the membrane modules. Total membrane module sales are currently about U.S. $200 million/year. The industry is extremely competitive, with the manufacturers producing similar products and competing mostly on price. Many incremental improvements have been made to membrane and module performance over the past 15 years, resulting in steadily decreasing water desalination costs in inflation-adjusted dollars. Some performance values taken from a paper by Dave Furukawa are shown in Tab. 7.2. Since 1980 the cost of spiral-wound membrane modules on a per square meter basis has decreased sevenfold. At the same time the water flux has doubled, and the salt permeability has decreased sevenfold. Taking these improvements into account, today's membranes are almost 100 times better than those of the 1980s. This type of incremental improvement is likely to continue for some time.

Currently, more than 90 % of the reverse osmosis market is the production of municipal drinking water and ultrapure industrial water. In the early days of the industry, many thought that the treatment of industrial process and effluent streams would be a major application. These applications did not develop, however, primarily because of low process reliability due to membrane fouling. A number of improvements that are likely to lead to greater use of reverse osmosis in these areas in the next few years are being made. Fouling-resistant membranes will help, and fouling-resistant module designs may be even more important. Vibrating or rotating modules in which the membrane is moved rather than the fluid flowing across the surface have proved able to treat extremely dirty solutions without fouling [4]. The design of one such system is shown in Fig. 7.3. Currently, these modules are extremely expensive – in the range

Tab. 7.2: Advances in spiral-wound module reverse osmosis performance (source: D. Furukawa, 1999).

Year	Cost normalized (1980 US$)	Productiviy normalized (to 1980)	Reciprocal salt passage normalized (to 1980)	Figure of merit*
1980	1.00	1.00	1.00	1.0
1985	0.65	1.10	1.56	2.6
1990	0.34	1.32	2.01	7.9
1995	0.19	1.66	3.52	30.8
1999	0.14	1.94	7.04	99.3

* Figure of Merit = (productivity) x (recip. salt passage)/cost

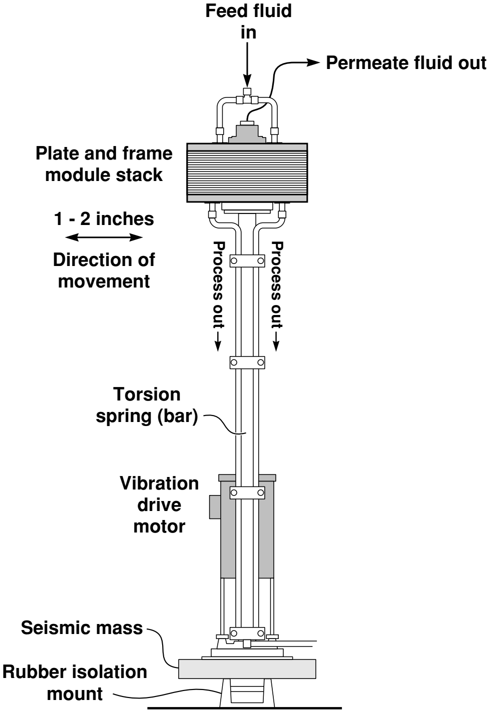
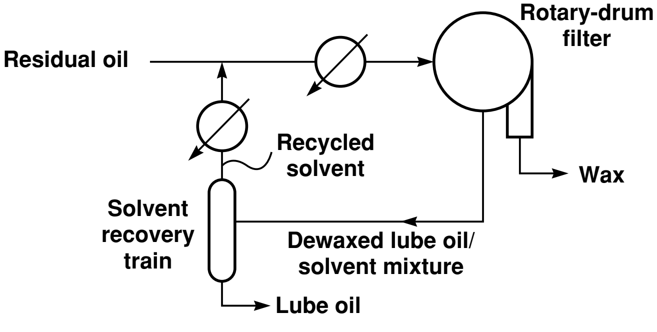


Fig. 7.3: New Logic International vibrating plate-and-frame module design. A motor taps a metal plate (the seismic mass) supported by a rubber mount at 60 times/s. A bar that acts as a torsion spring connects the vibrating mass to a plate-and-frame membrane module which then vibrates by 1–2 inches at the same frequency. By shaking the membrane module this way high turbulence is induced in the pressurized feed solution fluid that flows through the module. The turbulence occurs directly at the membrane surface, providing good control of membrane fouling [4].

\$2,000–5,000/m^2 – compared to alternative designs, which limits their applications. If costs can be reduced, a larger chemical industry market would open up.

A promising new application of reverse osmosis in the chemical industry is the separation of organic/organic mixtures. These separations are difficult because of the high osmotic pressures that must be overcome and because they require membranes that are sufficiently solvent resistant to be mechanically stable, but are also sufficiently permeable for good fluxes to be obtained. Nonetheless this is an area of keen industrial interest, and from 1988 to 1998 more than 30 U.S. patents covering membranes and membrane systems for these applications were issued.

One application that has already reached the commercial stage is the separation of small solvent molecules from larger hydrocarbons in mixtures resulting from the extraction of vacuum residual oil in refineries [5, 6]. Figure 7.4(a) shows a simplified flow


(a) Conventional solvent dewaxing process

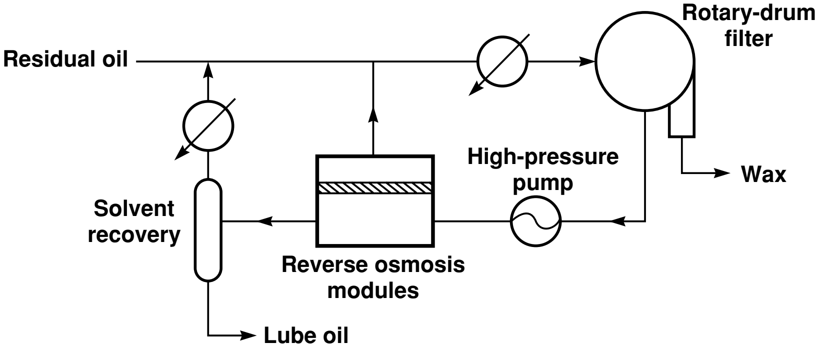

(b) Mobil Oil's solvent dewaxing process

Fig. 7.4: Simplified flow schemes of (a) a conventional and (b) Mobil Oil's membrane solvent dewaxing processes. Refrigeration economizers are not shown. The first 3-million gallon/day commercial unit was installed at Mobil's Beaumont refinery in 1998. Polyimide membranes in spiral-wound modules were used.

diagram of a refining lube oil separation process – these operations are very large. In a typical 100 000 barrel/day refinery about 15 000 barrels/day of the oil entering the refinery remain as residual oil. A large fraction of this oil is sent to the lube oil plant, where the heavy oil is mixed with 3 to 10 volumes of a solvent such as methyl ethyl ketone and toluene. On cooling the mixture, the heavy wax components precipitate out and are removed by a drum filter. The light solvent is then stripped from the lube oil by vacuum distillation and recycled through the process. The vacuum distillation step is very energy intensive because of the high solvent-to-oil ratios employed.

A reverse osmosis process developed by Mobil for this separation is illustrated in Fig. 7.4(b). Polyimide membranes formed into spiral-wound modules are used to separate up to 50 % of the solvent from the dewaxed oil. The membranes have a flux of 10–20 gal/ft^2 day at a pressure of 450 to 650 psi. The solvent filtrate bypasses the distillation step and is recycled directly to the incoming oil feed. The net result is a significant reduction in the refrigeration load required to cool the oil and in the size and energy consumption of the solvent recovery vacuum distillation section.

Mobil is now licensing this technology to other refineries. Development of similar applications in other operations is likely. Initially, applications will probably involve relatively easy separations such as the separation of methyl ethyl ketone/toluene from lube oil described above or soybean oil from hexane in food oil production. Long-term, however, the technology may become sufficiently advanced to be used in more important refining operations, such as fractionation of linear from branched paraffins, or the separation of benzene and other aromatics from paraffins and olefins in the gasoline pool.

7.2.2 Ultrafiltration

Abcor (now a division of Koch Industries) installed the first industrial ultrafiltration plant to recover electrocoat paint from automobile paint shop rinse water in 1969. Shortly afterwards, systems were installed in the food industry for protein separation from milk whey and apple juice clarification. The separation of oil emulsions from effluent wastewaters has also become a significant application. The current ultrafiltration market is approximately U.S. $200 million/year, but because the market is very fragmented no individual segment is more than U.S. $10–30 million/year. In the chemical and refining industries the principal application is the treatment of oily wastewater.

The key issue limiting growth of ultrafiltration is its high cost, because membrane fluxes are modest, large amounts of energy are used to circulate the feed solution to control fouling, membrane modules must be cleaned frequently, and membrane life times are short. These are all different aspects of the same problem – membrane fouling. Unfortunately, membrane fouling is an inherent feature of ultrafiltration. Only limited progress in controlling this problem has been made in the past 20 years and barring unexpected breakthroughs, progress is likely to remain slow. Better module designs, simple automatic backflushing, and inherently less fouling membranes are all being developed and used. Ceramic membranes, which are tougher and longer lasting than polymeric membranes, offer many advantages but are more than 10 times more costly than equivalent polymer membranes. Thus their use has been limited to small scale, high-value separations that can bear this cost. One area where ceramic membranes may find a future use is clarification of chemical or refinery process streams, where their solvent resistance is needed. However, it is difficult to see these applications becoming a major business unless costs are reduced significantly.

7.2.3 Gas separation

The first company to produce a successful gas separation process was Permea, now a division of Air Products, which introduced hollow-fine-fiber polysulfone membranes for the separation of hydrogen from ammonia reactor purge gas in 1980. This application was an immediate success – the gas was clean, free of condensable components that might damage the membranes, and the value of the recovered hydrogen provided short payback times. Within a few years many ammonia plants worldwide had installed these units. Several hundred hydrogen-separating systems have now been installed by Permea and its competitors.

Following this success, Generon, now a division of MG Industries, introduced a membrane process to separate nitrogen from air. The first-generation membranes had modest selectivities and were only able to produce 95 % pure nitrogen economically. By the late 1990s, Generon (MG), Medal (Air Liquide), Permea (Air Products) and IMS (Praxair) had all developed tailor made membrane materials with oxygen/nitrogen selectivities of 7 to 8 for this separation. These membranes produced 97 to 99 % nitrogen economically, so a large market for these systems, producing 10 thousand to 1 million standard cubic feet/day of nitrogen, developed. More than 10,000 of these systems have now been sold.

Other applications that developed in the late 1980s and the 1990s include separation of carbon dioxide from natural gas, separation of organic vapors from air and nitrogen, and dehydration of air. Table 7.3 lists the major companies involved in the industry and their principal products. Currently, total industry sales are estimated to be about U.S. $170 million. Of all the industrial membrane separation processes, gas separation is most closely linked to the chemical and petrochemical-refining industries, so its sales are affected by the chemical industry business cycle. In general, however, the trend for gas separation membranes is up, especially if some of the processes now being developed and described below are successfully introduced.

Hydrogen Refinery Applications: The separation of hydrogen from nitrogen, argon, and methane in ammonia plant purge streams was the first successful application of membranes. This separation and related separations such as hydrogen/carbon monoxide ratio adjustment involve separating hydrogen from clean gas streams free of condensable vapors. A larger application of membranes that exists in refineries and petrochemical plants is the recovery of hydrogen from gas streams containing condensable

Tab. 7.3: Current gas separation industry players. These sales numbers and market sizes are based on industry gossip and should be used with caution.

Company	Principal markets/estimated annual sales
Permea (Air Products) Medal (Air Liquide) IMS (Praxair) Generon (MG Industries)	The large gas companies are mostly focused on nitrogen/air (US$ 75 million/yr) and hydrogen separation (US$ 25 million/yr)
Kvaerner Separex (UOP) Cynara	Mostly natural gas separations (US$ 20 million/yr)
Whatman Ube GKSS Licensees MTR	Vapor/gas separation, air dehydration, other (US$ 25 million/yr)

gas mixtures. Figure 7.5 shows a typical application, the recovery of hydrogen from a low-pressure refinery fuel gas stream. Pressure swing adsorption (PSA) can separate hydrogen from this type of gas, but the cost of PSA scales in proportion to the amount of hydrocarbon that must be removed. In this case the gas contains 45 % hydrocarbon, and the PSA process would not normally be economical. Hydrogen-permeable membranes can easily perform this separation; the product permeate gas contains 93 to 95 % hydrogen. The process would be widely used except for the problem of condensation on the membrane. In the example shown in Figure 7.5, the dew point of the feed gas

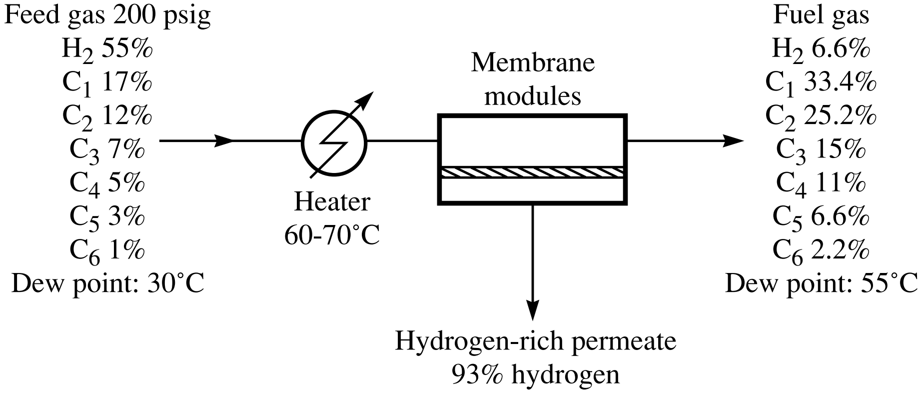
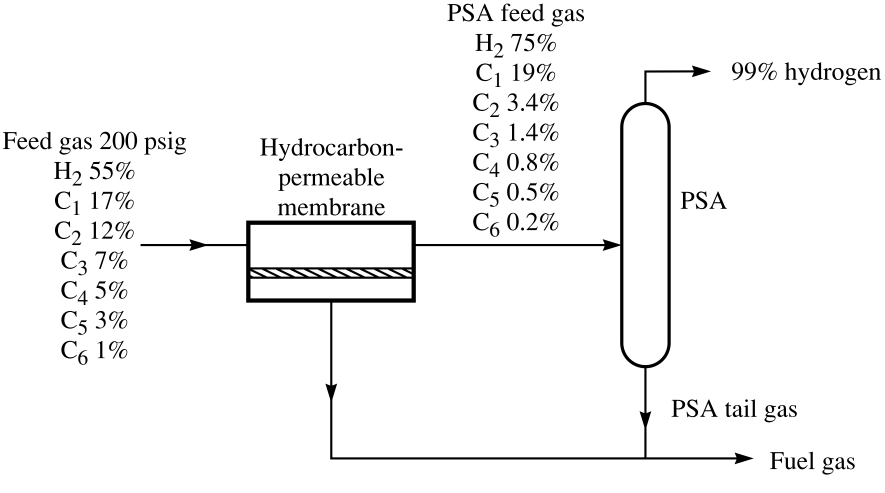


Fig. 7.5: Separation of hydrogen from refinery fuel gas with a hydrogen-permeable membrane. The feed gas must be heated to prevent condensation of heavy hydrocarbons in the membrane module.

is 30°C. As hydrogen is removed by the membrane, the gas stream becomes enriched in hydrocarbons and the dew point increases, reaching 55°C in the final residue gas. In industrial plants condensation of hydrocarbons on the membrane is prevented by heating the feed gas to 60–70°C. Provided the feed gas temperature remains above the dew point, condensation of hydrocarbon will not occur. However, even a transient plant upset producing a rise in pressure or a small increase in the concentration of C_5^+ components in the feed gas can increase the dew point by 10 to 15°C or more, causing hydrocarbon liquids to condense on the membrane surface and membrane failure. This type of reliability issue has prevented widespread acceptance of hydrogen-separation membranes in the refinery and petrochemical industries.

One solution to this problem, being worked on at Air Products with microporous carbon membranes [7] and at MTR with modified silicone rubber membranes [8], is to use membranes permeable to hydrocarbons rather than to hydrogen. Because the selectivities of these membranes are not as good as those of hydrogen-permeable membranes, the product hydrogen stream is not as pure and a significant fraction of hydrogen is lost with the hydrocarbon permeate. However, the hydrogen remains on the high-pressure side of the membrane so recompression is avoided.

An application for which hydrocarbon-permeable membranes are being considered is shown in Fig. 7.6. The hybrid process consists of a membrane system in front of a PSA unit used to produce pure hydrogen. The incoming feed gas has the same composition as shown in Fig. 7.5 but in this example a modified silicone rubber membrane preferentially removes the hydrocarbons, enriching the feed gas to 75 % hydrogen. Because hydrocarbons permeate the membrane, the feed gas becomes depleted in



Hydrogen recovery by membrane unit ~55%

Fig. 7.6: Combination process of hydrocarbon-permeable membranes and PSA to separate hydrogen from refinery fuel gas.

hydrocarbons and the dew point of the gas falls. These membranes have no problems with liquid condensation. The hydrogen-enriched residue gas might be used as produced in some refinery applications, but normally would be sent to a PSA plant to produce 99+% hydrogen. The membrane hydrogen-preconcentration step changes the hydrocarbon/hydrogen ratio of the gas fed to the PSA unit from 0.8 moles of hydrocarbon/mole of hydrogen to 0.3 moles of hydrocarbon/mole of hydrogen. This decreases the amount of hydrocarbon to be removed in the PSA polishing step significantly. These refinery hydrogen recovery processes are just now being demonstrated, but in the future this application could become large as refinery needs for hydrogen increase.

Oxygen/Air Separation: Various approaches to using membranes to separate oxygen from air have been investigated over the years. All rely on selectively permeating oxygen and rejecting nitrogen. Because air already contains almost 80 % nitrogen, and the nitrogen remains on the residue side of the membrane, it is comparatively easy to obtain essentially pure nitrogen from air. Nitrogen has been produced commercially using polymeric membranes since the early 1980s [9]. Producing oxygen by a membrane separation process is much more difficult because membranes that exhibit both high selectivity for oxygen over nitrogen (for good separation) and provide high transmembrane oxygen flux (to control costs) are needed. The process was developed to the early commercial stage in the late 1980s using silicone rubber [10, 11] and ethyl cellulose [12] membranes, but its performance and cost made it uncompetitive with other technologies.

Currently most oxygen is produced by cryogenic separation of air, at a cost of \$40–100/ton. This mature technology has been refined to the point at which major cost reductions are unlikely. A new alternative technology is vacuum swing adsorption, which is claimed to produce 90–95 % pure oxygen at \$40–60/ton. Membranes have the potential to reduce these costs substantially; as illustrated in Fig. 7.7, the target for a membrane process to make a significant impact is an oxygen cost of \$15–35/ton EPO_2.[1]

A simplified flow scheme of a membrane separation process to produce oxygen-enriched air is shown in Fig. 7.8(a). Feed air containing 21 % oxygen is passed across the surface of a membrane that preferentially permeates oxygen. In the scheme shown, the pressure differential across the membrane required to drive the process is maintained by drawing a vacuum on the permeate gas. The alternative is to compress the feed gas.

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[1] Cryogenic processes produce essentially pure oxygen whereas membrane and adsorption processes produce a lower-concentration oxygen product. To compare the economics of different processes producing different concentrations of oxygen-enriched air, oxygen costs in this paper are reported on an equivalent pure oxygen (EPO_2) basis. EPO_2 is defined as the amount of pure oxygen that must be mixed with normal air to obtain oxygen-enriched air at the specified concentration. For example, in a membrane process producing 40 % oxygen-enriched air, only the oxygen added in excess of the contained in air is counted, that is,

$$\left(40 - \frac{60 \times 21}{79}\right) or 24{,}1\%$$

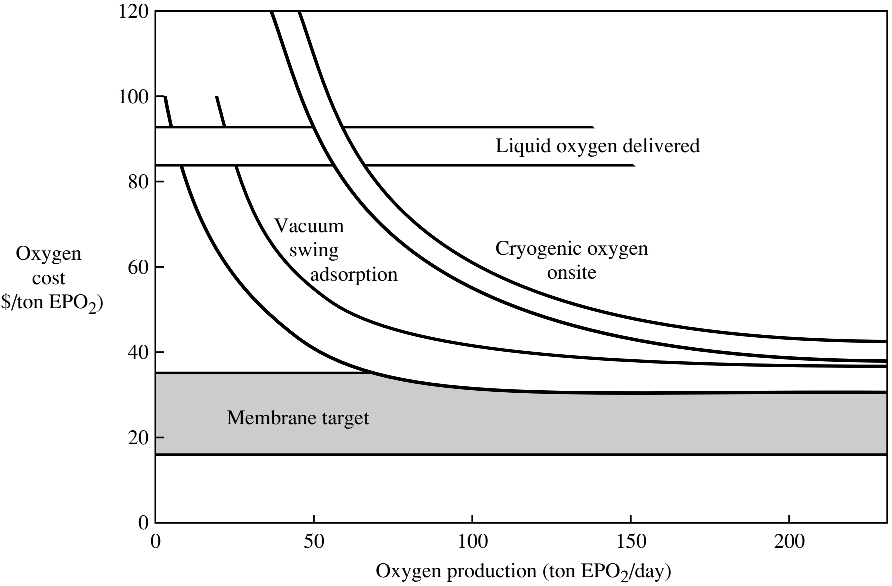
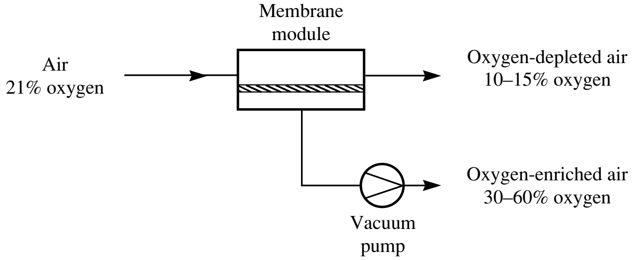


Fig. 7.7: Comparison of costs of producing oxygen with current technologies and the membrane target cost. Cryogenic on-site oxygen production falls with plant size, plateauing at about \$35–40/ton EPO2 for 500–1000 ton EPO2 capacity [13].

A few trial calculations show that a process using a feed gas compressor, even if coupled with an energy-recovery turbine on the residue side, cannot produce low-cost oxygen because of the quantity of electricity consumed. All the feed air must be compressed but only a small portion permeates the membrane. The power consumption of a vacuum pump is less because the only gas evacuated by the vacuum pump is the oxygen-enriched product that permeates the membrane.

Depending on the properties of the membrane and the pressure differential, a permeate gas containing 30–60 % oxygen is produced. Such oxygen-enriched air can be used in a number of processes, for example, in Claus plants and FCC catalyst regeneration in refineries or to more efficiently burn methane in high-temperature furnaces or cement kilns. Other processes may require an oxygen content of 95–98 %, for example, in a reformer to produce synthesis gas. The higher oxygen content can be achieved by adding a second separation stage as shown in Fig. 7.8(b). Because the volume of gas sent to the second-stage separator is one-quarter to one-third the feed to the first-stage unit and the gas is more concentrated, the second stage will be much smaller. This second separation stage could be another membrane unit or, more likely, a vacuum swing adsorption system, which will be more economical in this oxygen concentration range. The size and energy consumption of vacuum swing adsorption systems is almost a direct function of the nitrogen removal required because it is the nitrogen that adsorbs on the molecule sieve adsorption beds and must be removed with vacuum pumps. Starting

(a) One-Stage Membrane Separation Process



(b) Two-Stage Separation Process

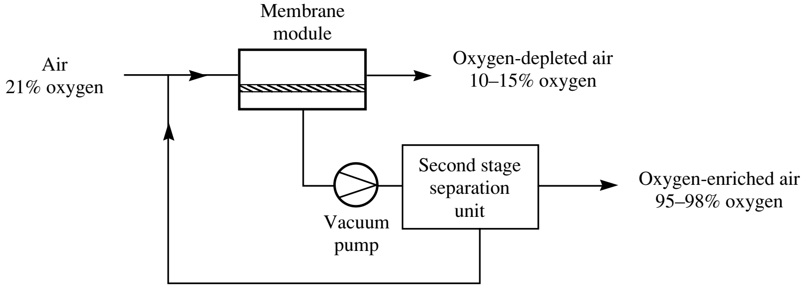


Fig. 7.8: Oxygen/air separation process designs: (a) one-stage membrane separation process, (b) two-stage separation process.

from 50 % oxygen (1 mole of nitrogen/mole of oxygen) rather than from 21 % oxygen (4 moles of nitrogen/mole of oxygen) reduces the mass of nitrogen to be separated per ton of oxygen product fourfold. The resulting cost of upgrading the gas from 50 % oxygen to 95–98 % oxygen is only \$10–15/ton EPO_2.

To achieve the process target costs shown in Fig. 7.7 very good membranes will be required. Figure 7.9 shows the estimated membrane performance required to produce 35–50 % oxygen in the \$20–25/ton EPO_2 range. These costs assume the capital cost of the vacuum pumps is about \$300/hp and membrane modules can be produced at \$5/m^2. Even with these aggressively low costs membranes significantly better than those produced today will be needed. Table 7.4 shows the properties of some of the very best membranes currently available for the separation of oxygen from air. The properties of these membranes are also plotted on Fig. 7.9. None are able to meet the \$25/ton EPO_2 target. It is also worth pointing out that the best hope for an economical process is likely to be membranes with selectivities of 4 to 5 and very high permeabilities. Much academic work is aimed at producing very highly selective membranes, but their permeabilities are low. Such membranes are unlikely to be optimum for this application or any other.

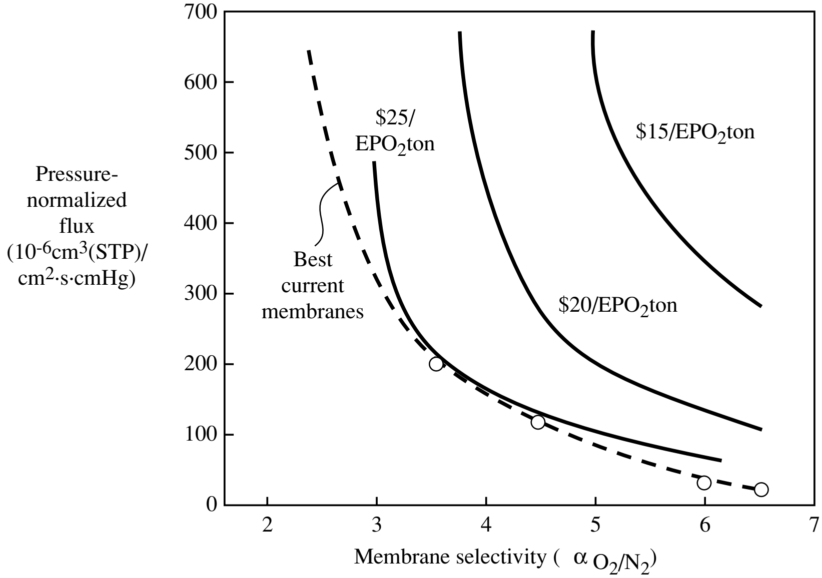


Fig. 7.9: Calculated oxygen production cost for 35–50 % oxygen as a function of membrane performance. The performance of some of today's best membranes is plotted on this curve.

Tab. 7.4: Properties of some of the best current oxygen/air-selective membranes.

Membrane material	Oxygen pressure-normalized flux ($10^{-6}cm^3$ (STP)/cm^2 s cmHg)	Oxygen/nitrogen selectivity
Silicone Rubber	1000	2.1
Ethyl Cellulose	200	3.5
Poly(phenylene oxide)	120	4.6
Permea Polysulfone	30	6.0
Generon Polycarbonate	20	6.5

Vapor/Gas, Vapor/Vapor Separations: Separation of light hydrocarbon vapors from each other, for example, propylene from propane, or separation of vapors from gases, for example, propane and butane from hydrogen or propylene from nitrogen, are major opportunities for membranes. A number of membrane plants have already been installed. For example, hydrogen-permeable membranes are being used in a number of refineries to recover hydrogen. Reliability problems caused by hydrocarbon condensation on the membranes has been a problem, but many carefully designed and operated plants have worked well for years. More recently, hydrocarbon-permeable membranes have been used to separate valuable hydrocarbons from vent streams [14, 15]. More than 20 units to separate and recover vinyl chloride monomer from nitrogen in poly(vinyl chloride) plants and 12 units to separate and recover ethylene and propylene from nitrogen in polyolefin plants are operating. However, the units installed thus far have only just tapped the potential membrane opportunity.

An example of the very large potential opportunity for this type of membrane gas separation processes is in the production of ethylene. Ethylene is the largest volume petrochemical – about 200 large crackers are in operation worldwide, each with an average production of about 1 billion lb ethylene/year. The recovery and separation of ethylene and other products from the cracked gas represents the majority of the capital and energy used in those plants. Currently, distillation is used, but the volatility of the gas mixtures to be separated means that high pressure/low-temperature distillation columns are required. Figure 7.10 shows a simplified flow scheme for a typical olefin plant separation train. The gas to be separated is very much a function of the cracker furnace operating conditions and the feedstock used. Table 7.5 shows some of the typical component distributions of the products of cracking [16].

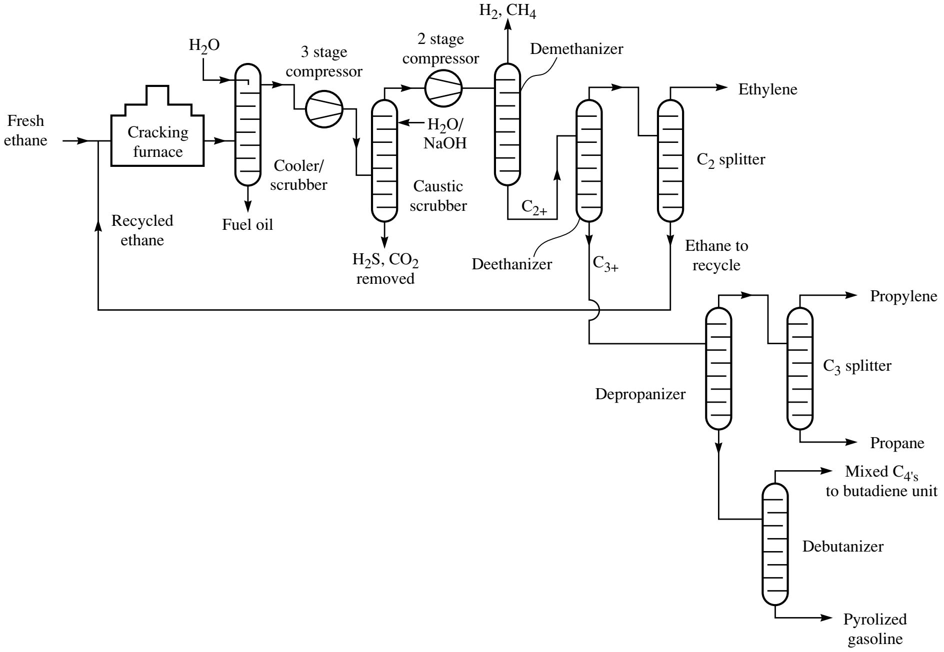


Fig. 7.10: Simplified ethylene cracker flow scheme. Multiple, large, low-temperature towers are used to fractionate the product gas mixture.

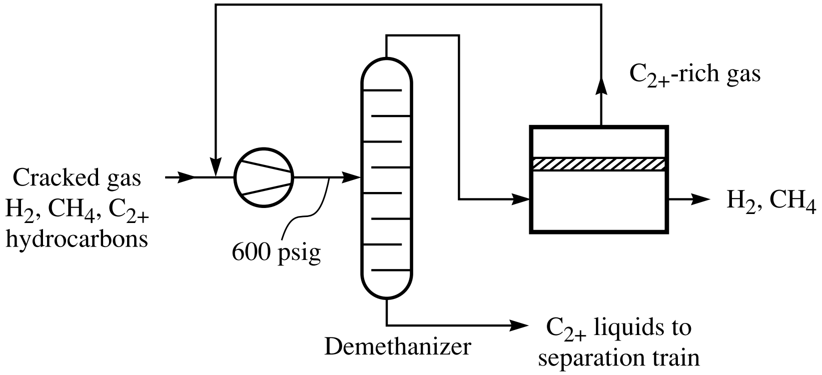
Table 7.5: Typical component distribution from various olefin generation techniques [16].

Process	**Steam cracking**			**Methanol to olefins**
Fedstock (excl. water)	**Ethane (C_2H_6)**	**Light naphta (boiling range 95–300°F**	**Atmospheric gas oil (boiling range 365–635°F)**	**Methanol (CH_3OH)**
Yields (wt%) (excl. water)				
H_2	3.9	1.0	0.6	0.03
CO	trace	trace	trace	0.49
CO_2	trace	trace	trace	2.46
CH_4	3.8	18.0	11.2	1.45
C_2H_2	0.4	0.95	0.4	0.0
C_2H_4	53.0	34.3	26.5	53.73
C_2H_6	35.0	3.8	3.4	1.67
C_3H_4	0.0	1.02	0.8	0.0
C_3H_6	0.8	14.1	13.4	26.37
C_3H_8	0.1	0.35	0.2	1.53
C_4H_6	1.1	4.45	5.0	0.0
C_4H_8	0.1	3.7	3.7	6.64
C_4H_{10}	0.2	0.1	0.1	1.21
C_5	0.2	2.75	2.7	3.37
C_6-Hg	0.3	1.2	1.2	0.88
Benzene	0.3	6.9	6.9	0.0
Toluene	0.0	3.2	3.2	0.0
Xylene + ethylbenzene	0.0	1.3	1.3	0.0
Styrene	0.0	0.79	0.7	0.0
C_9-400°F	0.0	2.96	2.9	0.0
Fuel oil	0.0	15.45	15.4	0.0
Carbon	trace	trace	trace	0.17
total	100.0	100.0	100.0	100.0

Olefin plants do not use distillation as their product separation method because this is a good application of distillation – quite the contrary. The initial demethanizer tower, for example, operates at 450 psig and uses – 100°C ethylene as a coolant. These conditions require special metallurgies, and essentially complete removal of water, carbon dioxide and hydrogen sulfide from the feed gas. Similarly, the C_2 splitter and C_3 splitter are massive towers containing 150 to 200 trays because of the very close boiling points of the ethylene/ethane and propylene/propane mixtures to be separated. Distillation is used for these separations because it is currently the only separation technique that works.

A number of opportunities exist for membrane separation units in these plants. The first large opportunities are likely to be in debottlenecking processes by using a membrane unit to perform an initial separation. This will reduce the load on the refrigeration plant or subsequent distillation operations. A number of authors have proposed schemes to use membranes to remove hydrogen and methane from the feed gas to the cracker cold train. This reduces the refrigeration load of the plant and, because the demethanizer can then operate at a higher temperature, use of special construction materials can be avoided. Two possible designs are shown in Fig. 7.11. In the first process, shown in Fig. 7.11(a), a silicone rubber or other light-hydrocarbon-permeable membrane unit is placed after the demethanizer column operating between –20 and –40°C [8]. Because the column is operated at a relatively high temperature, a portion of the ethylene/ethane components in the gas is lost with the overhead methane/hydrogen stream. The hydrocarbon-permeable membrane captures these components for recirculation to the front of the main compressor.

(a) Hydrocarbon-permeable/hydrogen- and methane-rejecting membranes



(b) Hydrogen-permeable/hydrocarbon-rejecting membranes

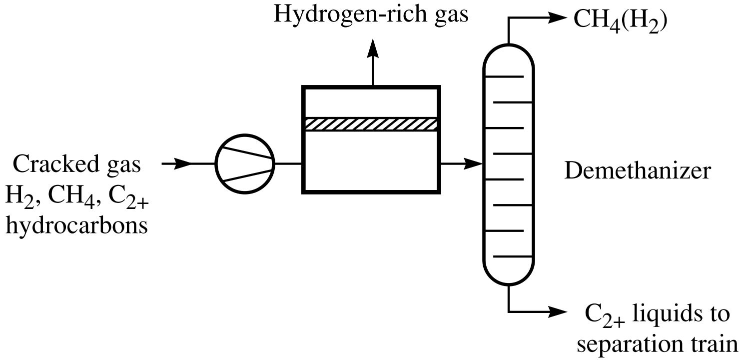


Fig. 7.11: Possible membrane/distillation process for ethylene cold train demethanizer.

In the design shown in Fig. 7.11(b), a polysulfone-polyaramide hydrogen-permeable membrane is used to remove hydrogen from the gas sent to the low-temperature demethanizer [17, 18]. In the stream composition shown in Tab. 7.5, hydrogen represents only a small weight fraction of the feed gas, but because its molecular weight is low it may represent 20–30 % or more of the volume of the cracked gas. Removing the hydrogen prior to the demethanizer makes the gas much more condensable, reducing the refrigeration load as well as producing a valuable by-product stream.

Another very large potential application of membranes in ethylene plants is replacing the C_2 and C_3 splitters. An example of a possible process design is shown in Fig. 7.12. In this example, a two-step membrane system equipped with propylene-permeable membranes is used to split a 50/50 propylene/propane overhead stream from a depropanizer column into a 90 % propylene stream and a 90 % propane stream. Both streams would then be sent to distillation units for polishing, but the size of columns required would be much reduced. For this design to be feasible, membranes with an olefin/paraffin selectivity of 5 to 10 are required. Many other designs that combine membranes and distillation columns to achieve good separation are possible [19].

Olefin/paraffin selectivities of 5 to 10 appear quite modest compared to the claims of some reports [20, 21]. However, much of the literature selectivity data have been calculated from the ratio of the permeabilities of pure olefin to pure paraffin. Olefin/paraffin selectivities measured with gas mixtures under conditions likely in a real process

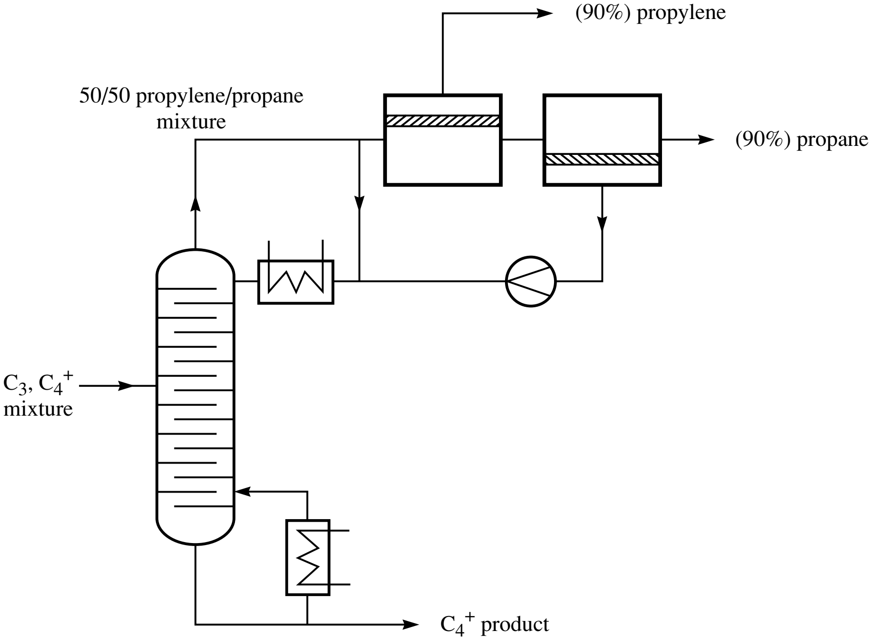


Fig. 7.12: Schematic of a propylene/propane membrane separation system installed on the overhead vapor from a refinery depropanizer column.

show that using pure gas permeabilities overestimates the membrane selectivity by a factor of 2 to 10. Therefore, it will be some time before olefin/paraffin-selective membranes are used in ethylene plants, although some nearer-term applications exist in petrochemical and refinery operations.

7.2.4 Pervaporation

The commercial success of pervaporation has been a disappointment to many process developers. Current pervaporation sales worldwide are probably less than U.S. $10 million; almost all are for dehydration of ethanol or isopropanol solutions using water-permeable poly(vinyl alcohol) or equivalent membranes. A smaller market also exists for the separation of volatile organics from water using silicone rubber membranes.

The historical development of pervaporation technology can be tracked by the number of U.S. patents issued each year that relate to pervaporation, as illustrated by the plot in Fig. 7.13. Prior to 1960, only a handful of patents had been issued on pervaporation, but beginning in 1960 a series of patents were issued to Binning, Lee and others at American Oil covering the use of pervaporation membranes to separate organic mix-

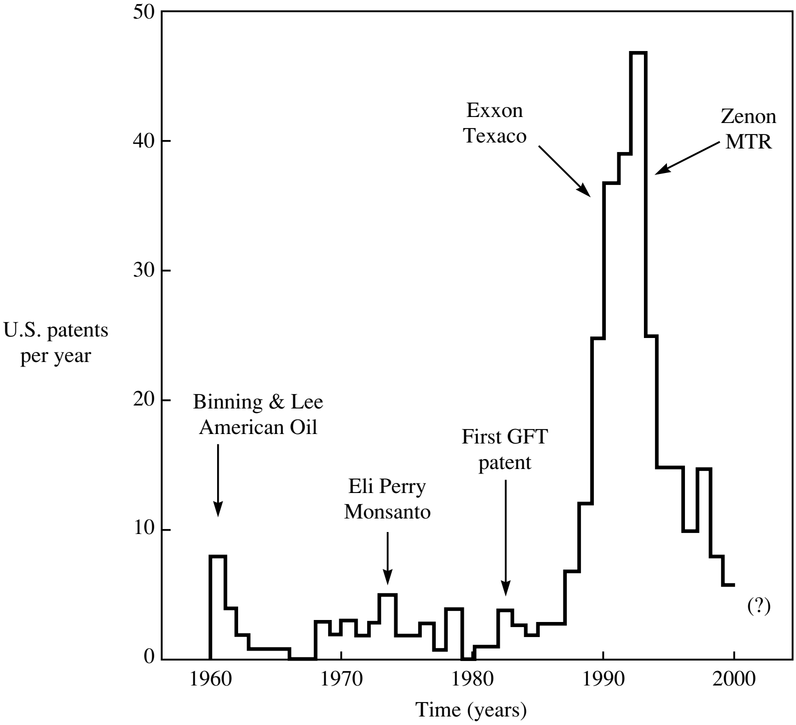


Fig. 7.13: Pervaporation-related U.S. Patents issued from 1960 to present.

tures, dissolved organics from water, and so on. Membrane technology was not sufficiently advanced to make these applications practical at that time, and American Oil abandoned the program after a few years. Through the rest of the 1960s and into the 1970s, a low level of interest was maintained in the process at Monsanto, Exxon and Standard Oil, principally with the hope of separating organic mixtures such as styrene/ethyl benzene. Interest in the process surged in the 1980s following the installation of the first solvent dehydration plants by GFT. At that time many researchers thought it would only be a matter of time before pervaporation would begin to replace distillation in large refinery and petrochemical applications. As a result research groups were established at Exxon, Texaco, Standard Oil, and elsewhere to develop the technology. The Exxon group in particular devoted considerable resources to developing membranes able to separate close boiling aromatic/aliphatic refinery mixtures. Membranes with toluene/n-octane separation factors of up to 10 were obtained, and the process was taken to the pilot scale. In practice, however, the technology was still not competitive with distillation, and by the mid-1990s most of the oil companies were closing down their groups.

Currently, only a handful of companies, Sulzer Chemtech, Ube, Mitsui and MTR, remain active in the area. The current market will no doubt expand over the next years, particularly in the food industry, where interesting opportunities to recover high-value flavor and aroma compounds from process and waste streams exist. The most promising large-scale application is still the separation of organic azeotropes and close boiling mixtures, but significant improvements in membrane selectivity will be required to make the process economically viable.

7.2.5 Ion-conducting membranes

In a discussion of future developments of membranes in the chemical industry a mention of the considerable effort now being made to develop ion-conducting membranes is in order. The overall concept is to use ceramic membranes that conduct oxygen ions at high temperatures. Materials that can conduct both oxygen ions and electrons are called mixed-conducting matrices. Various complex metal oxide compositions, including some better known for their properties as superconductors, have mixed conducting properties; recent efforts in this field appear to be focused on these materials [22, 23]. An example of this type of material is perovskites having the structure $L_{ax}A_{1-x}Co_yFe_{1-y}O_{3-z}$ where A is barium, strontium or calcium, x and y are 0 to 1, and the value of z makes the material charge neutral overall. Passage of oxygen ions and electrons is related to the defect structure of these materials; at temperatures of 800 to 1000°C discs of these materials have been shown to be extraordinarily permeable.

Two large consortia, one headed by Air Products and the other by Praxair/BP-Amoco, are developing the membranes. To date the work has been done with small ceramic tubes coated with 5- to 10-µm-thick films of perovskites or other ion-conducting materials. Typical sample areas are 20–30 cm^2. At the appropriate operating tempera-

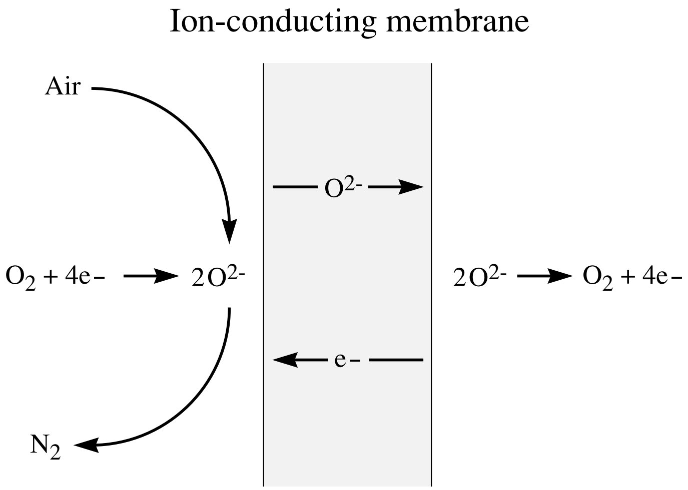


Fig. 7.14: The mechanics of mixed-ion-conducting solid state membranes.

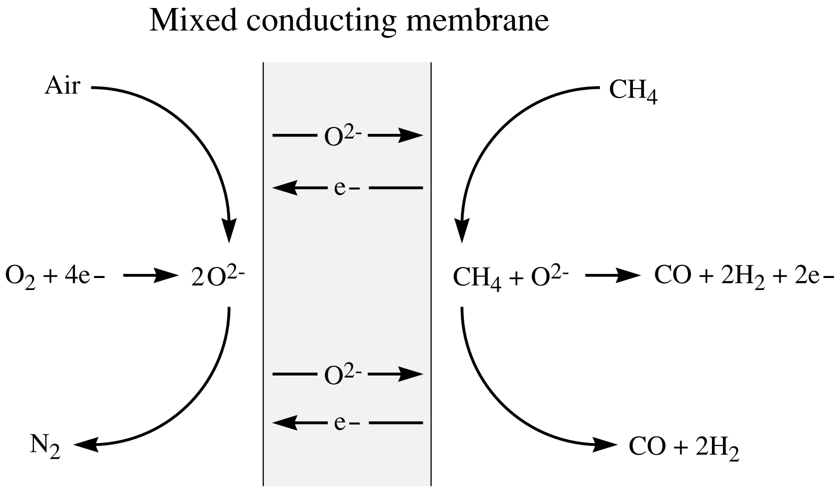


Fig. 7.15: Ion transport membrane-mediated partial oxidation of methane.

tures of 800–1000°C, the membranes are perfectly selective for oxygen over nitrogen, and oxygen permeabilities of 10 000 Barrer can be obtained. This means that if the membrane thickness can be reduced to 1 µm, pressure normalized fluxes of $10\,000 \cdot 10^{-6} cm^3(STP)/cm^2 \cdot s \cdot cmHg$ are possible. On this basis a plant to produce 1 MMscfh of oxygen will require about 4000 m^2 of membrane tube area – a large, but not inconceivably large, membrane area.

Although various schemes to produce oxygen from air using heat integration with power plants or steel mills have been proposed, the most practical application and the principal driving force behind the development of these membranes is the production of synthesis gas by the partial oxidation of methane, as shown in Fig. 7.15 [23]. Oxygen ions diffusing through the membrane react with methane to form carbon monoxide and hydrogen. This gas can then be used without further separation to form methanol or other petrochemicals. Will it work? It is difficult to know – certainly enough money is being thrown at the problem. The membrane areas involved are not huge but on the other hand, these membranes must be operated at temperatures of 800–1000°C; must be resistant to poisoning by other gases such as carbon dioxide, water, or sulfur compounds; must be defect-free; and must be able to withstand repeated thermal cycles from ambient to 1000°C. These are all serious technical challenges, but a major effort is being made to solve them.

7.3 The future: predictions for 2020

In 1983 I was hired as a consultant to predict development in the membrane separation area for the next 20 years. Looking at these predictions today, I find I was generally far too optimistic – sometimes ludicrously optimistic. I predicted that many refineries would be using pervaporation to separate organic mixtures by the year 2000 and that carrier-facilitated transport would be in use to separate oxygen from air. Neither of these has happened or is likely to happen in the near future. On the other hand, I grossly underestimated the success of membranes for the production of nitrogen from air. Despite this track record, I venture to show my predictions for 2020 in Fig. 7.16.

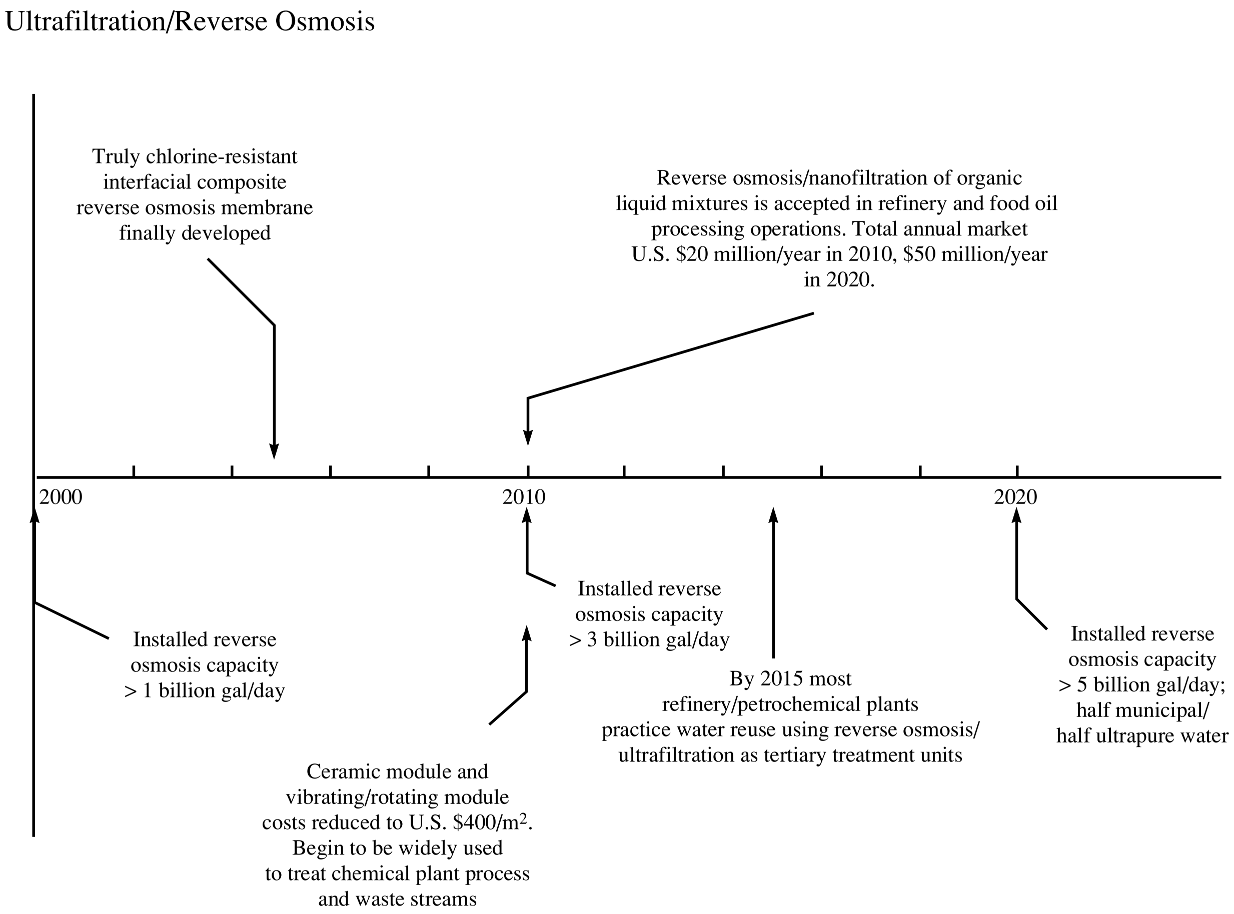


Fig. 7.16: Predictions of the development of membrane technology by 2020.

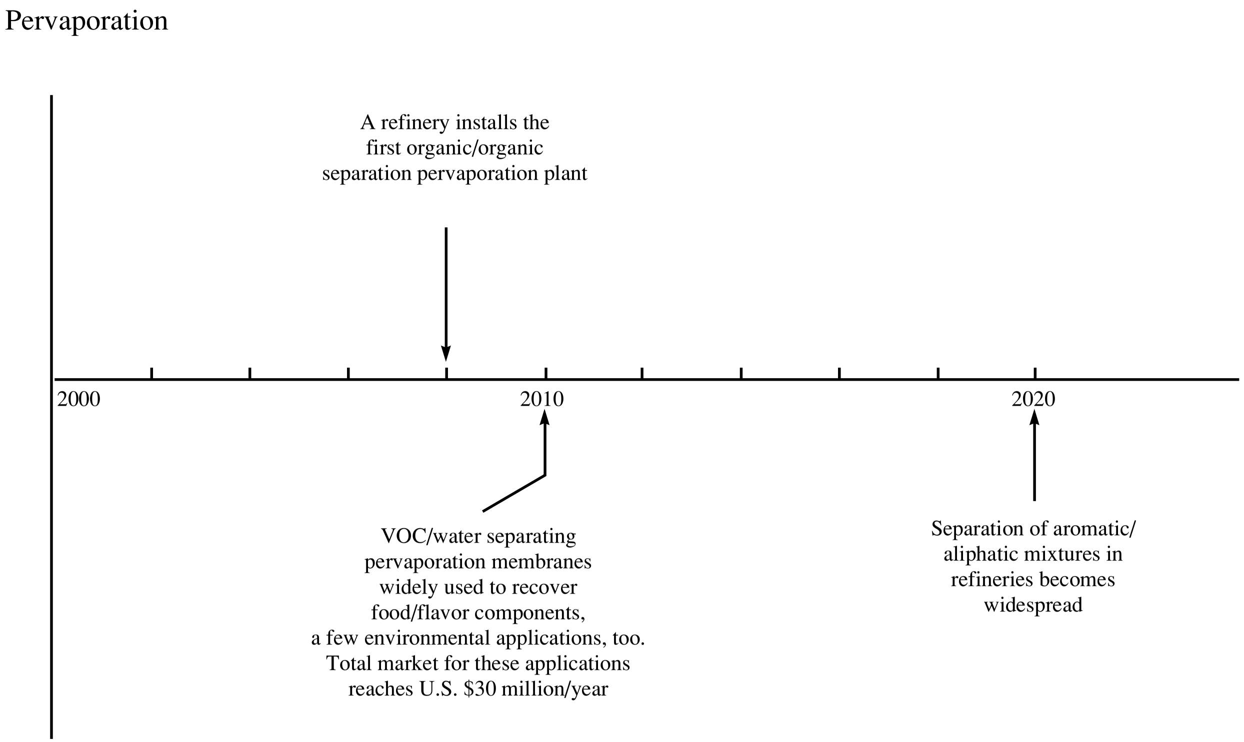


Fig. 7. 16: Predictions of the development of membrane technology by 2020 (continued).

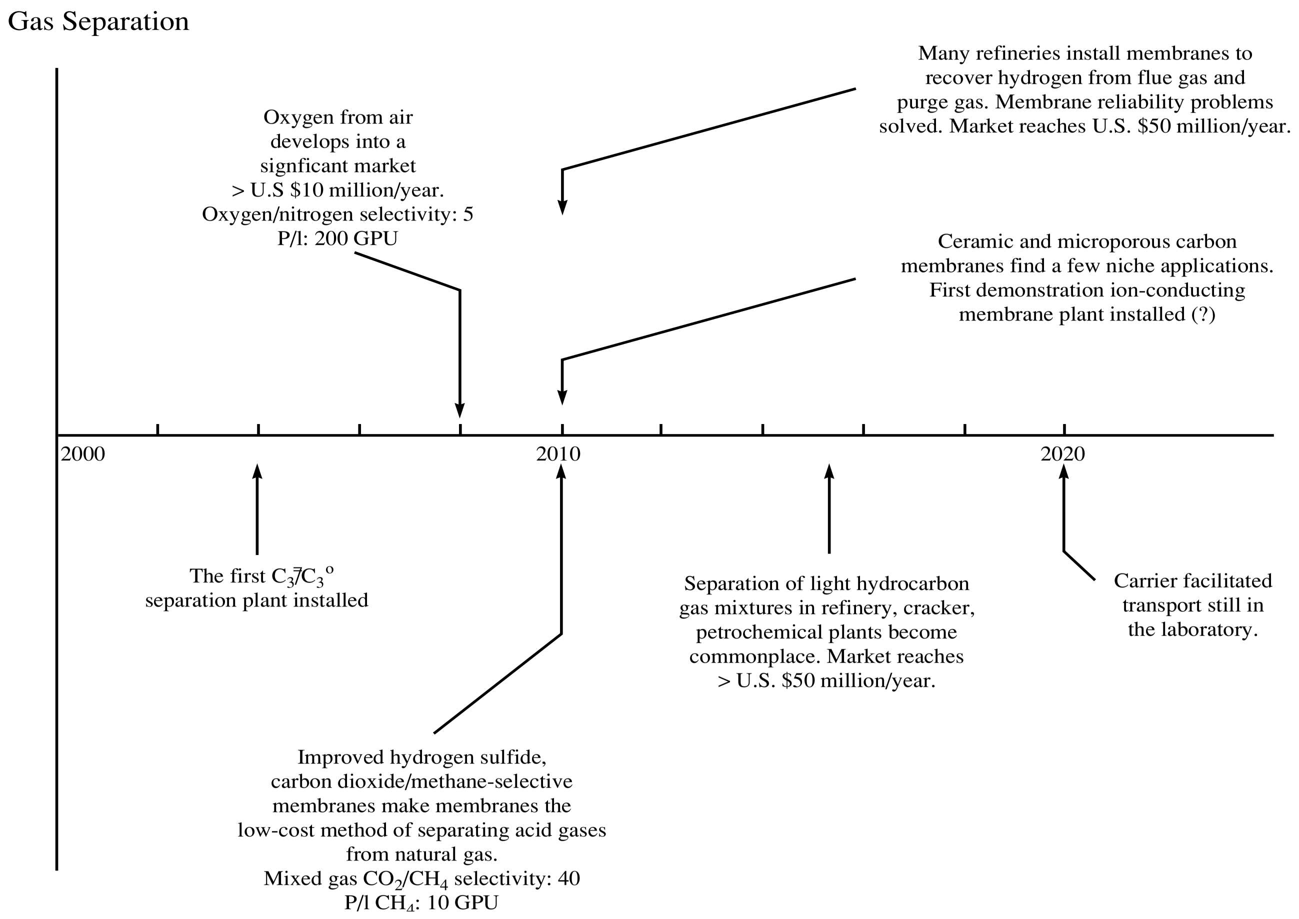


Fig. 7.16: Predictions of the development of membrane technology by 2020 (continued).

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