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Membranes in Chemical Processing a Review of Applications and Novel Developments

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MEMBRANES IN CHEMICAL PROCESSING
A Review of Applications and Novel Developments

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ABSTRACT

The recent development of membrane technology will strongly influence the way industry evaluates separation processes in the immediate future. In some fields membranes are already "proven technology" and incorporated in various production lines or purification processes; mainly within the food and dairy industries, water purification and treatment of liquid effluent streams. Smaller membrane modules for medical applications are also common, but large units in the chemical process industry are still rather rare.

This article gives a comprehensive overview of current applications, novel developments and potential for the use of membranes in selected industries within energy production, chemical process industry, wastewater treatment and gas purification. A brief summary for applications in industries like food and beverages, pharmaceutics and biochemical industry is also presented together with comprehensive references.

1. INTRODUCTION

The development of membrane technology will strongly influence the way industry is looking to separation processes in the future. In some fields membranes are already "proven technology" and incorporated in various production lines or purification processes. This is mainly within the food and dairy industries, water purification and treatment of liquid effluent streams. Small membrane units for pharmaceutical and medical applications are common, but large units in the chemical process industry are still rather rare. The current situation is due to several factors of both technical and economical kind. The lifetime of membrane material is crucial for the integration of membrane modules in industrial process streams which will usually transport fairly large volumes of gas and liquids at pressures and temperatures where the durability of the membrane materials over time are not yet fully exploited. If the membranes have to be replaced too often, the solution may be too expensive, or if the membrane is easily damaged it may be dangerous as well. First of all the basic question must be asked: Will the membrane solution work as well or better than the existing technology? This question has to be answered on the basis of product quality, energy consumption and environmental issues. Secondly: are the costs of this new technology currently at a level which will make the implementation attractive? Not until this is achieved for the various applications, will this technology have a significant technical breakthrough.

More than in any other field of separation, membrane technology demands that basic research within material science is coupled to the understanding of problems related to the specific industrial process where the membrane module is to be integrated. Too often research stops in a laboratory with experiments carried out under ideal conditions and over too short a time period, and results are reported as "interesting and promising" for a certain membrane. A stronger involvement of industry is often necessary in order to develop the membrane to commercial level, and thus promote the incorporation of membrane modules in a process together with other unit operations. The argument for doing so is the obvious advantages this technology offer: cleaner and simpler process solutions, less chemical additives, lower energy consumption.

The demand on industry for better environmental solutions and cleaner technology is thus pushing membrane technology into the spotlight. End-of-pipe solutions for purification of effluent streams will to a larger extent be substituted by closed systems with integrated process solutions in the future, resulting in simpler and cleaner industrial processes. Membranes are the solution nature itself uses for separation and purification - the technical challenge is to develop just as efficient synthetic membranes for the separation of industrial process streams.

A comprehensive profile of the international membrane industry was recently published by Elsevier Advanced Technology[1]. Besides giving an excellent overview of the world membrane market, it lists selected major membrane manufacturers and suppliers world wide.

In the present article attention is drawn to some salient examples of applications and novel developments for the use of membranes within the chemical process industry. According to the textbook of Shreve and Brink (Chemical Process Industries -77) [2], chemical process industry includes processes such as electrochemical, energy production, agricultural, food and diary, pharmaceutical, petrochemical etc. It is far beyond the scope of this article to cover all these industries as each topic alone could cover an entire article. The attention is therefore drawn to selected examples of applied membrane technology within a few fields: 1) energy production 2) chemical process industry 3) water and wastewater treatment and 4) gas purification. In addition a brief summary for applications in industries like food and beverages, pharmaceutics and biochemical industry is presented in a separate chapter together with references for more detailed information on these topics.

This article is addressing the topic of industrial membrane applications in a distinctly different way from that of a textbook on membranes. A textbook will naturally address the topic by looking at the different types of membrane processes and their driving forces, thus going into the type of transport mechanisms through the membranes and finally give examples of applications. In this article the various chemical process industries are in focus, and related membrane applications could thus be discussed under several sections. Here cross-references to various sections are given where multiple applications are relevant. A typical example would be the application of catalytic membrane reactors (CMR) which are relevant for many applications - here it is discussed under the section of dehydrogenation (3.1.3) and then referred to in other sections. Likewise, pervaporation processes are not handled as a separate topic, but illustrated with applications like dehydrogenation and removal of volatile organic compounds (VOC) in connection to relevant industries.

Each chapter has two main sections; *current applications* and *novel developments and potential*. The economics of the membrane processes are only in a few cases commented on, but it is fair to say that wherever membrane technology is currently applied, it has proven to be both a successful environmental and economical investment. Novel developments and potential are showing the trend for application of membrane technology within industry; for some of these developments there may still be a long way to go before the solutions are technological and economical acceptable.

Some producers are highlighted in the article for certain membrane applications; these producers are usually only a few out of many. The interested reader is advised to check relavant information in more detail[1]. Likewise the references to specific technology developments may not be complete, nor do the ones chosen necessarily represent the most significant advances at present. The membrane technology is developing very rapidly and this article can therefore only highlight part of it. In addition to the large number of scientific journals reporting membrane advancements in various categories, there are several good textbooks and handbooks on the topic. A comprehensive overview of industrial membrane processes is given in "The Membrane Handbooks" of Ho & Sirkar[3] and Scott[4].

Only a very general conclusion on the applications and perspective for industrial membrane applications is presented at the end of the article as each section has a "stand-alone" discussion on current applications, novel developments and potential. Certain concepts and expressions may not be familiar to all the readers. These are marked with a star* and are defined at the end of the article in alphabetic order.

2. ENERGY PRODUCTION

Energy production in the world today is concentrated within five main areas: coal, hydro-electric, nuclear, natural gas and oil. The main part of this energy production is still based on fossil fuels (see Figure 1[5]). The world energy consumption is expected to increase dramatically over the next ten years, but the global mix of fuels will change only slowly. Thus the global problem of environmental pollution and the exhausting of valuable resources is immediately put into focus for our attention. Combustion of fossil fuels produces sour gases and carbon dioxide; the sour gases produce acid rain, and the carbon dioxide production adds strongly to the greenhouse effect. It is of vital importance to encourage the implementation of membrane solutions; a technology which has the potential both to reduce energy consumption of fossil fuels and at the same time present a cleaner process solution.

This section will focus on the potential and use of membranes in the oil and gas industry, both for production of energy as well as for purification of gas streams. Membrane fuel cells and examples for minor applications such as energy production from biogas will be handled separately.

2.1 OIL AND GAS INDUSTRY

2.1.1 Background

Oil and gas production involves a series of unit operations suitable for integrating membrane modules. This covers many different aspects, from the production of blanketing gas (N_2) for the oil and gas production system, removal of sour gases (CO_2, H_2S), drying (removal of H_2O vapor from the natural gas) and to separation of hydrocarbons to produce sales gas with specified heating value (Wobbe index*). Membrane separations are well suited for this type of separation because natural gas is typically available at high pressures (30 - 80 bar) which gives a favorable driving force across the membrane (with increasing permeation flux at increasing pressures).

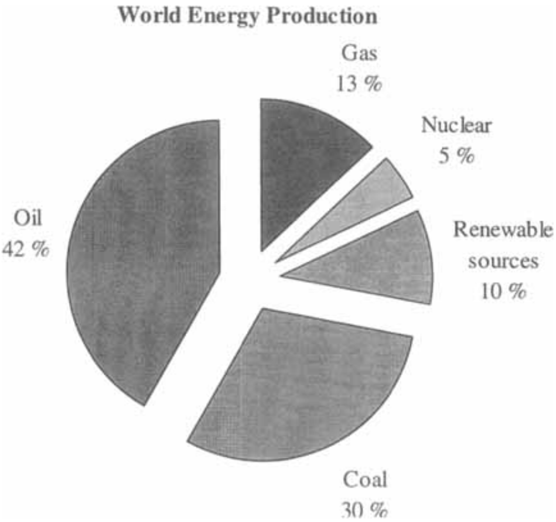

FIGURE 1 Contributions to world energy production by types of fuels and renewable sources ("World Resources -93")[5]

The fast permeating components are typically CO_2, H_2O and H_2S; thus CH_4 is concentrated in the retentate (on high pressure side) without a significant pressure drop. The crucial question will be the selectivities of the various materials for the permeating components compared to CH_4, and the necessary membrane permeation area to perform the specified separation. There are commercially available modules for this type of separation, and the material is typically made from polyimide hollow fibers or cellulose acetate spiral-wound membranes. Their performance have been evaluated as acceptable in the processes where they have been installed to date. Future development for the application of membranes in the oil and gas producing industry will most probably focus on polymeric materials with selective carriers for the components to be removed, the development of membranes for the separation of hydrocarbons. Hybrid membrane processes combining different types of membrane units are also one of the development trends.

2.1.2 Current Applications

a) High Purity Nitrogen

High purity nitrogen must be available at production sites for oil and gas; it is used for purging of pipelines and blanketing of equipment. Today the production of pure nitrogen from air by the use of membranes is considered proven technology, and modules are available from several producers (Ex. Permea, Dow, Linde, Medal) The separation is often done by the use of hollow fiber membranes with materials of polysulphone (PS) or poly(phenylene)oxide (PPO). Detailed information on these membrane solutions for air separation can be found in many references[6,7].

b) Membrane Units for Gas Dehydration

Membrane units for gas dehydration on a large scale were not available until recently. Permea Maritime Protection has now reported successful development of a patented solution in several papers[8,9] - this is discussed in the section "Novel Developments". These modules are not yet fully commercialized; but the first full scale demonstration unit is installed at a site for a major oil company. These membrane dryers are expected also to find applications for the drying of air or gas streams in industry. Membrane gas dehydrators have been on the market for about ten years, but these modules are for small gas streams and mainly air drying (Scott, sections 3 & 5)[10] Membranes that efficiently remove CO_2 and H_2S will in general also remove $H_2O_{(vap)}$.

c) Membranes for Removal of Acid Gases (CO_2, H_2S)

Acid gases (CO_2, H_2S) must be removed from crude natural gas prior to its use in order to

-increase the heating value
-reduce corrosion during transport and distribution
-prevent atmospheric pollution

The removal of acid gases (mainly CO_2) from crude natural gas and offgases by the use of membranes has received much attention for economic and environmental reasons. The amount of CO_2 in natural gas is typically in the range of about 10% by volume or less; the gas is at very high operating pressures (35 - 80 bar) and the specifications for removal of sour gases are very strict when producing sales gas. The application of membrane units will depend upon the scale of operation. The membrane solutions found at sites today will typically handle low to moderate gas volumes and, quite often, the separation process is a hybrid solution with membranes combined with traditional technology. The membrane modules in operation are typically made from polyimide or polysulfone hollow fibers or asymmetric cellulose acetate (CA) (flat sheet or spiral wound modules). The CA membranes show higher selectivity between the CO_2 and CH_4 compared to the other two types, but must operate at fairly low temperature (preferably below 50^0C or 122^0F). The hollow fiber configurations will typically handle larger volumes of gas compared to the spiral-wound modules due to the higher packing density (permeation area per unit volume). Recovery of CO_2 in the oil and gas production is of major importance when it comes to promote enhanced oil recovery (EOR) from depleted fields: High pressure CO_2 is pumped back into the reservoir at the periphery of the field and diffuses through the formation to drive residual oil toward the wells. The recycled gas generally needs to have a purity of at least 95% CO_2. In these EOR-processes hybrid solutions with membrane modules in combinations with amine absorption is often preferred.

Examples of membrane processes for CO_2 removal:

There are several membrane units in operation around in the world today based on the proven technology developed (amongst others) by Dow, Grace Membranes and Hoechst.

- Membrane technology has been used for enhanced oil recovery (EOR) at smaller fields for more than ten years. One of the earliest (and largest) membrane plants for EOR was the SACROC unit in West Texas which started up in 1984. The hollow fiber membrane units are owned and operated by Cynara, a subsidiary of Dow. In this process the purified CO_2 stream from the membranes is further treated with hot potassium carbonate prior to reinjection into the oil field. A single membrane stage is used followed by multiple banks of membrane permeators in parallel, thus plant performance can be optimized under varying feed conditions by adjusting the number of permeators in operation[10]. Over the years the CO_2 content of the associated gas production from the field has increased from 0.5 mol% CO_2 up to a level of app. 60 mol% CO_2. The inlet gas conditions were pressure 35 bar (515 psi) and a temperature of 94^0C (201^0F). The normal hydrocarbon product from Cynara facility has app. 30 mol% CO_2 at 32 bar (480 psi) and a temperature of 10^0C (50^0F)[11]

- Membrane test facilities were also started up at a low-quality natural gas well in East Texas in 1994. This unit is different from the one mentioned above; it is a commercial single-scale single-stage spiral-wound* membrane system. Tests were performed with varying CO_2 concentrations in the feed (6 - 25 mole%), and throughout the test period the retentate product (the sales gas) met pipeline specifications. Two types of cellulose-acetate (CA) membranes were tested; one of standard quality and one of higher density, and the effect of various operating variables (pressure, feed flow rate and CO_2 conc.) on the separation were studied[12]. In general, the stage cuts* for both membranes followed the same dependence on the pressure, feed flow rate and CO_2 concentration in the feed. High CO_2 stage cuts were necessary to reduce the CO_2 concentration in the retentate product to in order meet the pipeline specification (2 mole% CO_2) without having too high a methane loss. No measurable deterioration in the membrane performance, aging or hysteresis was noticed.
- Comprehensive theoretical studies are performed by Bhide and Stern showing the influence of process configuration, feed composition and operating conditions using membrane processes for the removal of acid gases from natural gas [13,14]. The economic of the membrane process will greatly depend on the these parameters as can be seen from Figures 2 and 3 shown as an example:

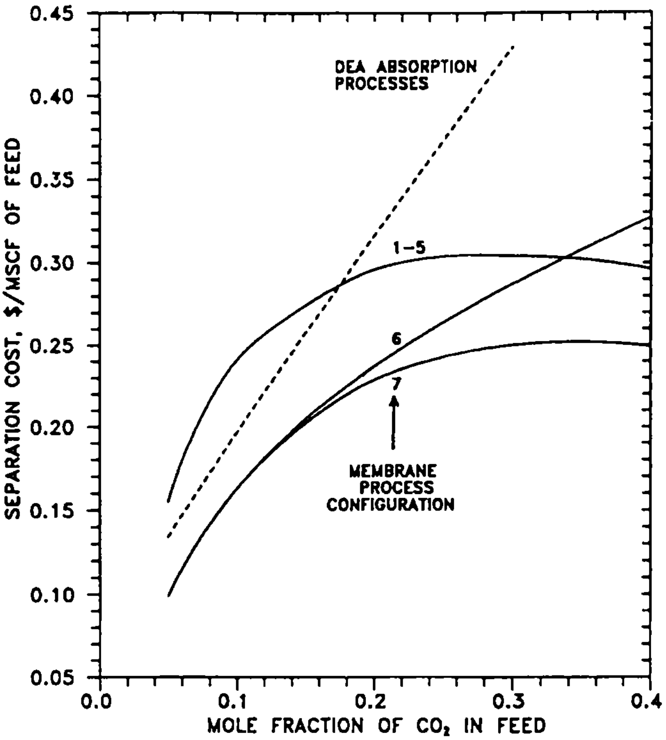

FIGURE 2 Comparison of CO_2 removal from natural gas by membrane and DEA (diethanolamine) gas-absorption processes. Base-case operating conditions in Table I.

Curves 1-4	RRF=0.0	where	RRF = ratio of recycle to feed
5	RRF=0.0, FNF=1.0		FNF =fraction of net retentate contributed
6	FNF=1.0		by the retentate from first stage
7	FNF=1.0		

(Bhide and Stern [14]*, reprinted from J. Membr. Sci., 81, p. 289, Copyright© (1993) with kind permission from Elsevier Science)*

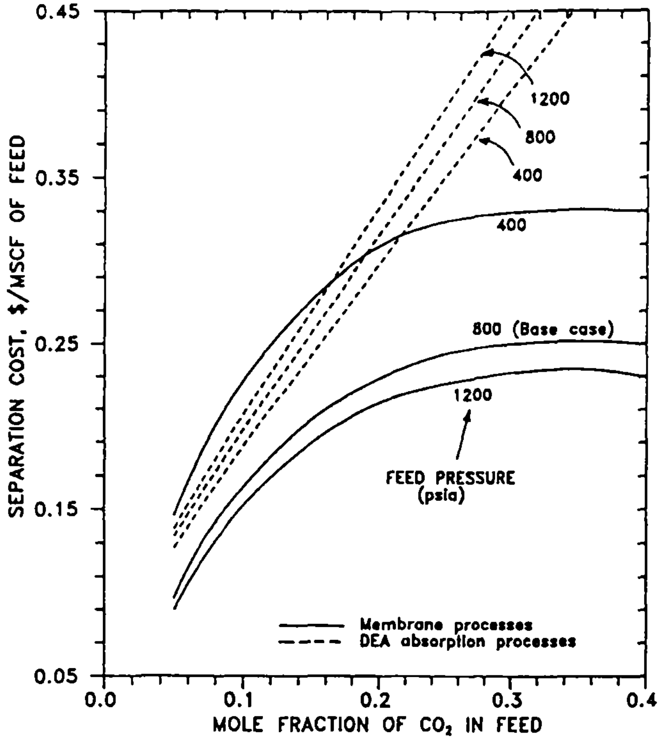

FIGURE 3 Effect of feed pressure on the cost of CO_2 removal from natural gas. Other operating conditions are given in Table I
(Bhide and Stern [14], reprinted from J. Membr. Sci., 81, p. 289, Copyright© (1993) with kind permission from Elsevier Science)

Figure 2 shows the effect of separation costs as a function of mole fraction of CO_2 in the feed stream for seven different module configurations compared to a standard gas absorption process with diethanolamine (DEA) in an absorber with a subsequent stripping unit. The base case operating conditions are given in Table I. The numbers on the curves refer to the following seven different module configurations:

1. single stage membrane module
2. single stage with retentate recycle

TABLE I

Base Case Operating Conditions

for the membrane processes illustrated in figures 2 and 3 (Bhide and Stern[14])

Feed (sour) gas flow rate	35×10^6 std.ft^3/day*	(1×10^6 m^3(STP)/day)
Feed Composition	5-40 mole% CO_2, 1 mole% N_2 1 mole% C_2H_6, balance CH_4	
Retentate* composition	< 2 mole% CO_2	
Effective membrane thickness	$\delta = 3.94 \times 10^{-3}$ mil	(1000Å)
Pressure of feed stream	800 psia	(54 bar)
pressure of permeate stream	20 psia	(1.4 bar)

*The retentate ("sweet gas") flow rate will depend on the concentration of acid gases in the feed ("sour gas"), the operating conditions, the permeator configuration and the properties of the polymer membrane used.

3. two permeation stages in series with permeate recycle
4. two permeation stages in series with retentate recycle
5. two permeation stages in cascade arrangement with permeate recycle
6. two stage membrane process in cascade arrangements with retentate recycle
7. single stage in series with two stages permeation cascade

As can be seen from the Figure 2, the configuration 7 (shown in Figure 4) seems to be the most efficient process. If the evaluation of a membrane solution for the process would have been based on the separation of a single stage unit, or even the first five configurations, the membrane alternative would have been ruled out as interesting. However, good engineering coupled with an understanding of how the membrane performs, leads to the attractive alternative of configuration 7. For example for CO_2, concentrations of 10, 20 and 30 mole% in the feed stream, the separation costs for the number seven process are respectively 17, 28 and 41 % lower than those for conventional DEA absorption processes. By contrast, the separation cost for a single

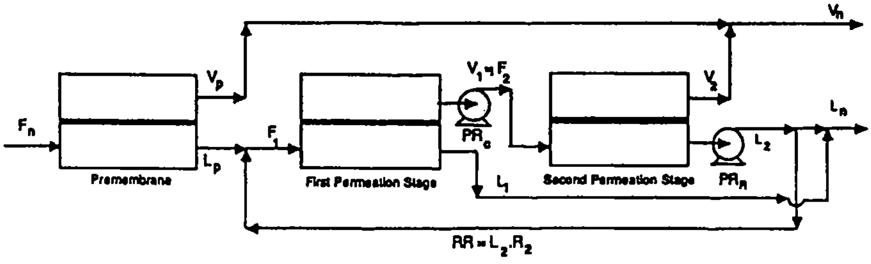

FIGURE 4 Configuration 7 (with reference to example in text); single permeation stage in series with two-stage permeation cascade
(Bhide and Stern [13]*, reprinted from J. Membr. Sci., 81, p. 209, Copyright© (1993) with kind permission from Elsevier Science)*

permeation stage (config. 1) is lower than that of DEA gas absorption processes only at CO_2 concentrations higher than about 17 mole% in the natural gas feed.

Figure 3 shows the effect of feed pressure on the cost of CO_2 removal from natural gas (operating conditions are given in Table I). For the membrane processes, an increase in the feed pressure has the following effects[14]:

1. An increase in the partial pressure difference of CO_2 across the membrane, which is the driving force for CO_2 permeation
2. A decrease in the membrane area and power requirement
3. A decrease in the hydrocarbon losses
4. An increase in the fraction of CO_2 removed by the "premembrane" stage (see Figure 4); i.e. the fraction of net product (here permeate) contributed by the stage before the cascades and a decrease in recycle fraction due to lower hydrocarbon losses.

Consequently, at a specified concentration of CO_2 in the feed, the separation cost for membrane processes decreases with an increase in the feed pressure. By contrast, the separation cost for the DEA gas absorption processes increases slightly with increasing feed pressure.

Membrane processes for the removal of H_2S

Whenever CO_2 is removed using membranes and H_2S is present in the feed stream, the latter will permeate together with CO_2. This is also the situation when H_2S is present and the gas is dried with membranes. The specifications for removal of H_2S in the product gas stream is typically down to < 10 ppm; this is usually no problem if the concentration of H_2S is < 50 ppm in the feed. A separate membrane solution for the removal of H_2S seems not to be economical at present. There are however promising results reported from ongoing studies to selectively remove H_2S from CO_2. By using a weak acid/base interaction of H_2S and methyl-di-ethanol-amine (MDEA) the transport of H_2S through the membrane was found to increase compared to CO_2, thus resulting in higher selectivity[15,16]. Research reported from experiments with catalytic ceramic membranes are looking at the possibility of splitting H_2S into hydrogen and sulfur.

It should be mentioned however that most hydrogen sulfide can efficiently be removed before or after a membrane module by placement of a degassing tower[17]. When degassing is done before the membranes, calcium hypochlorite or chlorine is added to oxidize residual hydrogen sulfide and collodial sulfur formed to sulfate. To avoid the possibility of sulfur generation and formation of colloids that can foul the membranes, air stripping of the hydrogen sulfide from the permeate stream is used.

2.1.3 Novel Developments and Potential

a) High Purity Nitrogen

Membrane modules for high purity nitrogen production from compressed air have been proven technology for many years. Novel developments for this application are mainly within module design and on-site production of nitrogen for various purposes.

b) Membranes for Gas Dehydration

Polymeric Membranes

Natural gas has to be dried in order to prevent water from freezing or hydrates to form in pipelines for the gas distribution net. The potential for the application of membranes for natural gas dehydration is very large. There is a lot of ongoing research for membrane development, but so far only a few successful units are reported for commercial use on large scale. Permea Maritime Production (a division of Air Products) is one of the main producers of these membrane modules. Sweep gas is required to remove moisture efficiently in the membrane dehydrator. The effect of the sweep gas is reducing the partial pressure of water vapor on permeate side; thus increasing the driving forces across the membrane. The sweep gas introduced to the dehydration membrane may be nitrogen generated in a separate air fed membrane module (see Figure 5 for illustration) or dry product gas. The amount of sweep gas required will vary with the saturation temperature of feed, the operation pressure and the specification for moisture in the final product. For the high capacity - high pressure applications, the wide variety in targeted applications has given rise to requirements for varying sweep rates. Thus a fourth port is introduced so that sweep volume can be manipulated by conventional, process control systems[18].

Successful field tests have been carried out both at the "Sinni" plant located in South Italy (operated by S.P.I. a subsidiary company of Agip), and at Easington terminal in the UK (operated by BP Exploration). These two membrane system of Permea has been designed to treat up to 300.000 Nm^3/d natural gas at 70 barg (1000 psig), down to -20^0C (-4^0F) water dew point[9,19]. The results so far are very promising, and deterioration of the membrane does not seem to be any problem as long as liquids are removed from the gas by pretreatment. The first commercial unit is presently being installed and will be operated in the Norwegian sector of the North Sea.

Required water removal duty will have a significant impact on the weight and cost of a membrane dehydration system, whereas for the standard drying process with glycol

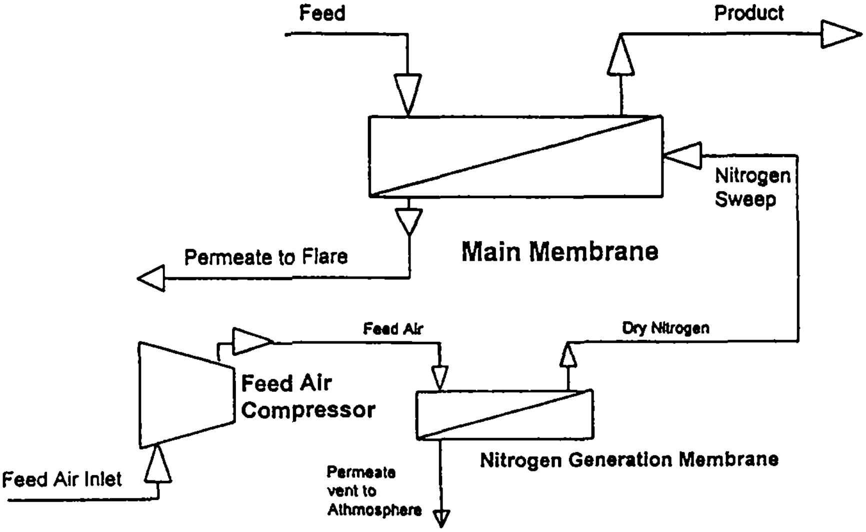

FIGURE 5 Membrane dehydration process using nitrogen as sweep gas (Johannessen and Jones [18])

regeneration (with tri-ethylene-glycol, TGE) the system is only to a minor degree affected by this. (For the membrane system the required permeation area is strongly dependent on the water removal duty.) This is illustrated in Table II. As can be seen, for moderate dewpoint depressions (30^0C or 85% water removal) the membrane equipment cost is expected to be lower than for TEG. This comparison does not include sweep gas generation or recovery. The weight ratio is strongly in favor of the membrane solution.

There are already numerous polymers available with very high selectivities for water vapor; 500 - 2000 are beneficial. The challenge for the membrane developments is the preparation of thin-film composite membranes* with ultrathin top layers. The water permeance should preferably be at least 30 m^3/m^2 h bar. The problem is of course that with increasing selectivity at a given water vapor flux, the necessary membrane permeation area also increases. This is illustrated for chosen process conditions in Figure 6[20].

TABLE II

Comparison of cost and dry weight per unit capacity for gas dehydration membranes versus standard drying process with TEG[18]

	TEG*		Membrane + Pretreatm.	
% Water removal	< 90%	95%	85%	95%
Cost ratio of equipment	1	1.1	0.8	1.2
Weight ratio of equipment	1	1.1	0.55	0.8

TEG = tri-ethylene-glycole; a standard chemical used for dehydration of natural gas

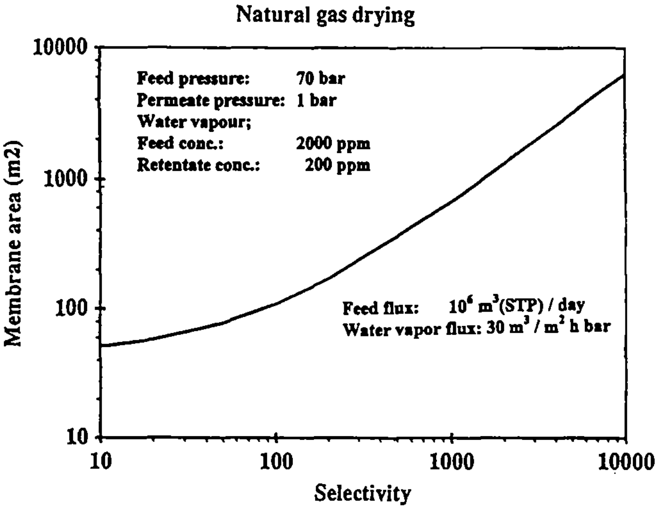

FIGURE 6 Natural gas drying process: Membrane area as function of selectivity for a given water flux. Process conditions given in figure (Peinemann [20])

Molecular sieve filters using zeolite membranes for gas drying:

Zeolites have been used for many years as an adsorbent in a wide range of industrial applications because of the regular and controllable pore sizes within their crystalline structure. The highly hydrophilic nature of the membrane means that water is always preferentially absorbed. Regeneration is then necessary when the adsorbent is fully loaded; this is usually done by thermal swing adsorption (TSA) or pressure swing adsorption (PSA). Due to its inorganic nature, the zeolite membrane is unaffected by many organic components that would ordinarily attack polymeric membranes. Zeolites are thus very attractive for drying operations and breaking of azeotropes. Comprehensive experimental studies report promising development within this field of membranes [21,22] Several producers are continuously working on improving the quality of these sieving membranes[23]. At present it is difficult to imagine that the zeolite membranes will become an alternative for drying of large volumes of gas or air - the necessary permeation area will be too large and the solution too expensive compared to traditional dehydration units or the polymeric membranes described above.

c) *Membranes for Removal of Acid Gases*

*Removal of CO_2 by the use of Facilitated Transport Membranes**

There are already commercial membrane units available for natural gas treatment (see previous section). The polymeric materials used today are mainly polyimides or cellulose acetate, and a cost efficient membrane process usually demands a CO_2 content higher than 13%. Although these materials exhibit fairly high selectivities for the gas separation in question (CO_2/CH_4; usually between 15 -35, for some new (not commercial) polyimides even up to 70), the selectivities and permeation flux is still too low when large amounts of gases are to be treated; the required permeation area will in general be too large. A more efficient separation is required, and the next generation membranes for this purpose will most probably be either materials with selective (fixed site) carriers, or selective absorbents in a membrane contactor.

It is well known that amines can react reversibly with CO_2, and this has been utilized in systems with the amine as a mobile carrier (selectivities up to 600 have been obtained). The stability of these amines are limited however, and the membranes have therefore never been used in technical applications on industrial scale. *Facilitated transport** of CO_2 through supported liquid membranes of aqueous amine solutions are reported by Teramoto et al as well[24]; and the permeation rates under various process conditions examined. The development of *fixed site carrier membranes** (FSCM) will typically be based on covalently bounded amine carriers in a polymeric material - thus the resulting membrane should exhibit the mechanical strength of the original polymer and hopefully have a much higher selectivity than the standard material[25]. Matsuyama and Teramoto use a functional membrane prepared by plasma grafted polymerization with amines as carrier[26]. Their membrane is in principle a cation-exchange membrane made by grafting acrylic or methacrylic acid to substrates such as polyethylene and polytetrafluoroethylene. The research is quickly moving forward for the development of these FSC-membranes; promising results are expected to be published. The theory for the transport mechanisms are excellently described by Noble in several publications [27-30].

The other competing technology for the removal of CO_2 from natural gas is the application of membrane contactors described below. This technology is about to be commercialized, but the technology is probably still a bit immature for application to large natural gas streams with fairly low CO_2 content (< 10 mol%). The development of membrane contactors has so far focused on the removal of CO_2 from flue gases. The advantages of this technology compared to ordinary gas separation membranes for CO_2 removal is well documented by Feron et al[31].

Removal of CO_2 by the use of Membrane Contactors

The focus on the global problem associated with the green house effect due to human activities and energy consumption based on fossil fuel combustion has challenged scientists to address the problem of CO_2. Removal of CO_2 from flue gases with the use of membrane contactors has been much in focus over the last years, and the technology of a gas liquid contactor (by chemical or physical absorption) is well known today, but only small units are presently commercialized. Typical solvents for absorption of CO_2 are shown in Table III. Much attention has been paid to the absorption rates for CO_2 of the various solvents since this will strongly influence the economics of the process when larger gas volumes are to be handled. A competing technology to membrane contactors will be facilitated transport membranes described in previous section.

The basic principle for a membrane absorption process is shown in Figure 7[3]. The membrane is typically a microporous material where the gas phase is either at a slightly lower pressure (here hydrophobic membrane*) or a slightly higher pressure (here hydrophilic membrane *) than the liquid. For a hydrophobic membrane the gas-liquid interface is thus at the pore mouth at the liquid side of the membrane, and as long as the excess aqueous solution pressure is less than the break through pressure, the aqueous solution will not penetrate the pores. Likewise for the hydrophilic membrane; the excess gas phase pressure must be less than the break through pressure in order to avoid gas bubbling into the aqueous solution. This type of membrane contactor is also often referred to as an "artificial lung" since the way it is functioning is the exact same as the way our blood is oxygenated and CO_2 removed through our lungs. Once the CO_2 is removed from the gas stream by absorption, there is however the question of regenerating the absorbent (by stripping) and disposal of the CO_2 in a suitable way. On offshore platforms this may easily be solved by reinjection into the reservoirs, but for smaller installations onshore or removal from various flue gas streams, other solutions must be found. One future solution may be to utilize the CO_2 enriched gas for instance in the horticultural industry.

The mass transfer of CO_2 from the bulk phase of the gas to the bulk phase of the liquid (amine solution) is described by several researchers [32,33,34], and, in general, the mass transfer coefficient, k (m/s), will be somewhat lower in the membrane modules

TABLE III

Typical solvents for the absorption of CO_2 *(Scott, p.281)*[4]

Chemical	Monoethanolamine (MEA) Di-ethanolamine (DEA) Tri-ethanolamine (TEA) Hot Potassium Carbonate Methyldiethanolamine (MDEA)
Physical	Methanol (Rectisol) N-methyl-2-pyrrolodone (Purissol) Polyethylene Glycol (Selexol) Propylene Carbonate (Fluor Sovent)
Physical / Chemical	Sulfolane/Di-isopropanolamine/Water (Sulfinol)

than in traditional separation towers due to the resistance across the membrane and the gas- liquid films. The advantages of a membrane contactor compared to traditional absorption column with random or structural packing, is that the compact membrane unit will have very high contact area per volume ("a"-value; m^2/m^3) and the possibility of independently varying the gas and liquid velocities.. The absorbent liquid has to be regenerated in a separate stripper which may also be a membrane-based contactor. Example: The Norwegian company Kvaerner, is on the brink of starting up a large scale prototype membrane contactor at Kaarstoe in 1998, with a scheduled commercial module in year 2001. Their membrane process is developed in co-operation with Gore, and their modules are made from a GORE-TEX® ePTFE microporous hollow fiber membrane. The pilot tests have so far proved successful for the membrane absorber unit, but the desorption through a membrane is more challenging due to the process conditions. The basis for the Kvaerner process is to

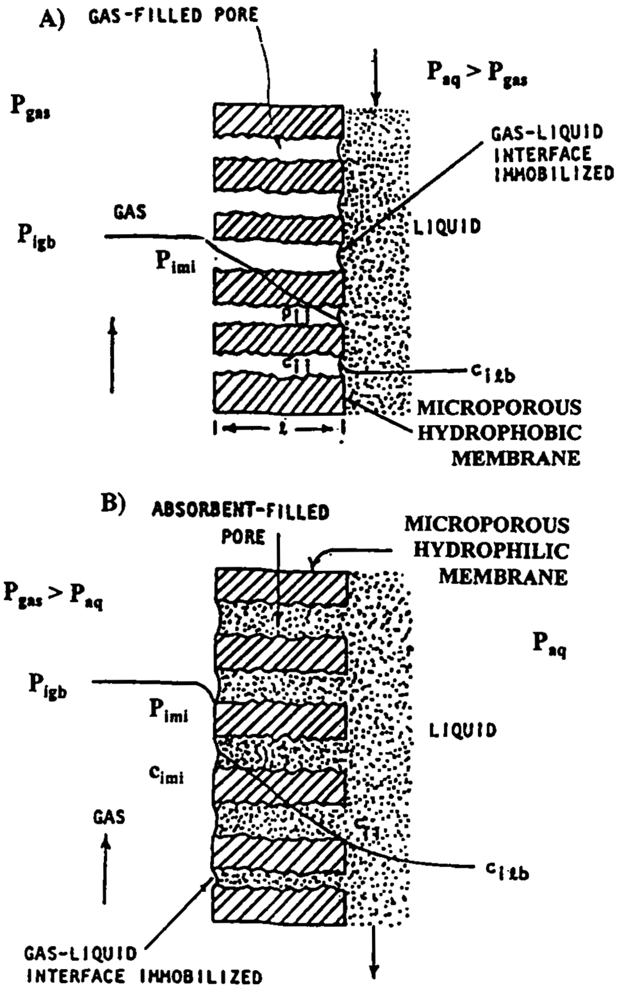

FIGURE 7 Basic principle of membrane absorption using a membrane contactor: Solute partial pressure and concentration profiles in gas absorption through a gas/liquid interface immobilised at the pore mouth of a microporous a) hydrophobic membrane with gas-filled pores and b) hydrophilic membrane with absorbent filled pores (Sirkar, p.886 [3])
(Index "ibg " = component i in bulk phase of gas; index "imi" = component i at membrane interface, index "ilb" = component i in liquid bulk phase)

use the membrane contactor in combination with a combined cycle power generation (gas turbine) unit with 40% recycling of the exhaust gas and a CO_2 compression unit. CO_2 could then be disposed of by injection back into the reservoir. An overview of the selected process is shown in Figure 8, and, as can be read from the figure, the energy and environmental potential of this process solution is very promising[35]. When evaluating the economics of a process solution for the recovery of CO_2 from flue gas, it is important to consider the extra energy necessary for the disposal of CO_2 back into the aquifer. At an offshore platform with combined cycle power generation and heat recovery this energy will easily be provided; but for onshore facilities this problem must be specially addressed[36].

It should be remembered that membrane solutions for removal of CO_2 from various gas stream; from natural gas, from flue gas, from landfill gas or effluent gas streams may demand very different systems. The removal of CO_2 is therefore also addressed in other sections of this article.

2.2 BULK HANDLING OF OIL - MEMBRANE APPLICATIONS

The removal and recovery of organic vapors from contaminated gas streams by means of membrane separation is finding increasing importance. There are more than 50 commercial vapor recovery units (VRU) in operation around the world today. The largest application is in the area of recovery of hydrocarbon vapors from off-gases emitted from gasoline tank farms; the smallest applications are units to treat off-gases generated by car refueling at gasoline stations. For handling of larger gas streams, the VRU's are often combined with pressure swing absorption - an example of a typical hybrid process is shown in Figure 9. The membrane process shown in the figure, is coupled to a tank farm, and the off-gas is collected in a gasometer. The liquid ring compressor (operating with gasoline as service liquid) sucks the hydrocarbon contaminated air from the gasometer. For a VR-unit with capacity around 1000 m^3/h, feed pressure around 3.5 bar absolute and suction pressure (permeate side) around 0.2

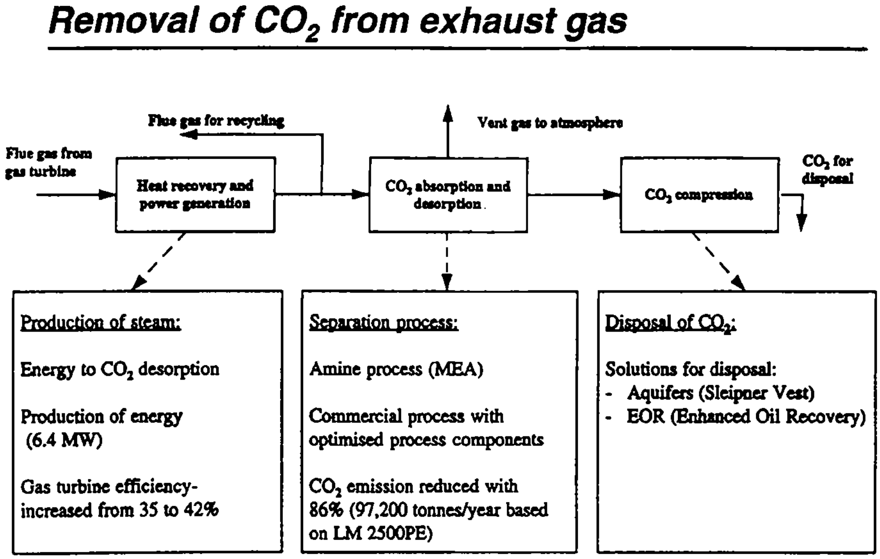

FIGURE 8 Schematic flowsheet of the Kvaerner process for removal of CO_2 from exhaust gas (Falk-Pedersen and Dannström [35])

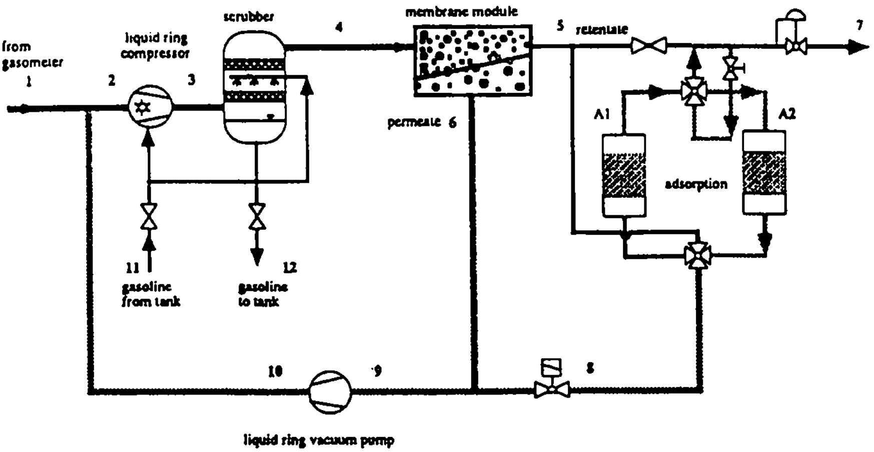

FIGURE 9 Flowsheet for a vapour recover unit (VRU) combined with pressure swing absorption (PSA) for removal of volatile organic compounds (VOC). The membrane process shown in figure is coupled to a tank-farm, and the off-gas is collected in a gasometer. (Ohlrogge et al[148])

bar, the membrane permeation area is typically around 140 m^2. The standard selective coating for the composite membrane used is polydimethylsiloxane (PDMS) - other elastomers can be selected. The membrane modules applied for this type of separation are a spiral wound modules or the "GS"-module (designed and patented by GKSS[37].) Up until now, most of the VRU installations have been "end-of-pipe" solutions. The potential for installation of solvent selective modules in chemical and petrochemical process streams is great however, and many integrated membrane solutions will probably appear in future. Separations involving removal of volatile organic compounds (VOC) from liquid and air streams in general is discussed under the relevant sections (Chap. 4 and 5).

2.3 ENERGY FROM BIOGAS

2.3.1 Background

A major contribution from the gases causing the green house effect (CO_2, CH_4, CFC) comes from landfills for households and industrial waste, and it seems obvious that human activity is emitting more of these gases than natural processes can remove. A comparison of the increase of these gases in the atmosphere with estimated anthropogenic* emissions finds that about 44% of the CO_2, 17% of the CH_4 and 100% of the CFCs represent net addition to the atmosphere[5]. In order to compare the effect of the various gases, a so-called "global warming potential" (GWP) is estimated with reference to CO_2. Calculations done by the UN Climate Panel states that one metric ton of CH_4 has a GWP 21 times larger than that of CO_2, while one ton of CFCs have GWP's from 6000 to 30,000 times larger!

The methane produced in the landfills is basically a large energy resource, and the potential of utilizing this energy is far from exploited. The gas from landfills consist of CH_4, CO_2, N_2, O_2, H_2, H_2S, H_2O (vap), and various odor gases in the ppm or ppb level. The landfill is mainly producing CO_2 during the first 3-4 years. Then the production of CH_4 rapidly increases, and a potential process for energy production may start. The typical cycle of a landfill is shown in Figure 10[38] and a possible

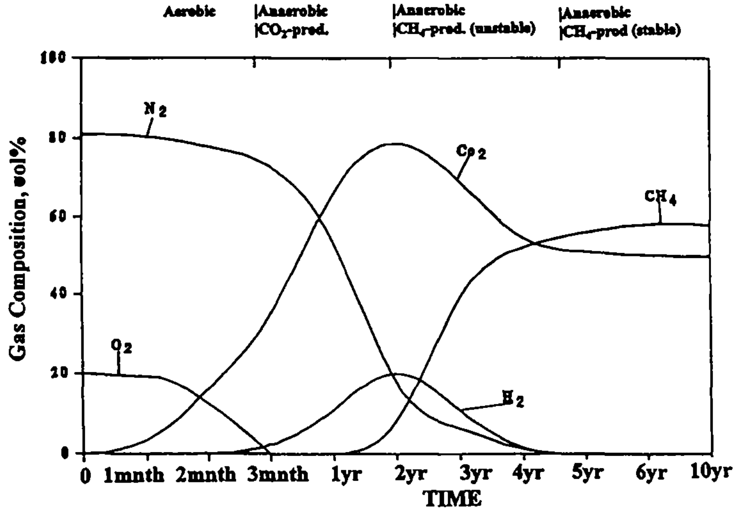

FIGURE 10 Typical cycle of the gas production in a landfill; composition of gas as function of time. (Halmoe [38])

arrangement for the conservation of the energy and harmful wastes is shown in Figure 11[38]. As can be seen from Figure 10, the gas composition at the start of energy production will be approximately around 50 mol% CH_4. Toxic trace components must be separated out if the gas is not going to be burned. About 3200 m^3(STP) / hr of biogas can be collected from a medium-size-dumpsite which is equivalent to about 1700 l/hr of fuel oil. The standard way of utilizing this energy around the world today (if at all considered) is by burning the gas on site in combination with a turbine and thus producing energy. This may be sensible if the energy distribution net is easily available, and for a small to moderate size landfill the production facilities and investments will then be acceptable. This way of utilizing the landfill gas will not necessarily need a membrane unit in the production line, however filtration and units for odor removal are essential. There are however better environmental solutions to this problem than just burning the gas on-site. These solutions are discussed in more detail below.

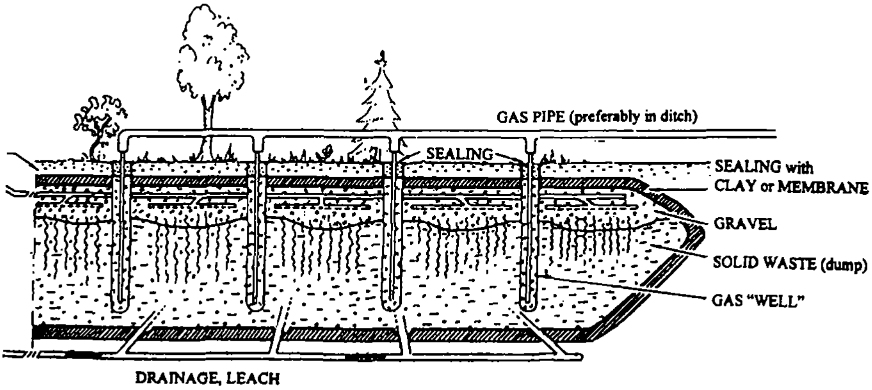

FIGURE 11 A typical arrangement for conservation of energy (gas) from a landfill and prevention of pollution (leaches) to soil and groundwater. (Halmoe [38])

Biomass from wastewater treatment will also produce methane. By sensible treatment of the biomass this solid waste may be processed to valuable energy - this is discussed in section 4.3 under Wastewater Treatment.

2.3.2 Applications and Novel Developments

The resources of fossil energy are unequally distributed throughout the world, and much research has been put into the development of alternative energy sources. One of these resources world wide is the biogas produced in landfills and biomass from sewage treatment (the latter is discussed in the section wastewater treatment). National potential for growth is often defined by the energy resources.

The common situation is still that the biogas is not utilized at all - then the CH_4 and CO_2 from the landfills are simply leaking into the atmosphere and adding to the greenhouse effect. This is about to change. When the biogas is utilized for energy production today it is usually being burnt on-site and produced energy is transported to the costumers. A more sophisticated solution is to produce compressed natural gas (CNG) or liquefied natural gas (LNG) from this biogas produced in landfills[39].

(The specifications of the gas will then be appr. $CH_4 > 95\%$, $CO_2 < 50\text{-}100$ ppm, $H_2O < 1$ppm). CNG and LNG are perfect fuels especially within public transportation like buses and ferries. The process solution demands a terminal for storage or filling station in connection to the production site. So far this utilization of the biogas has not received too much attention, but, with the current status of both the environmental problems related to the green house effect and increasing energy demand, the utilizing of the landfill gas in small efficient units may again come into focus. In The Netherlands, this seems to be accepted technology - they have already a few process units installed.

Example: Rautenbach (1994)[40] reports results from a pilotplant at a landfill in Germany which in '94 had been running for two years. This plant produces synthetic natural gas. The process consists of an adsorption stage for the toxic trace components and a membrane stage (with five modules Ube-polyamide hollow fiber) for the removal of CO_2. In Figure 12 the energy balances of three other processes are compared to the membrane process with respect to their individual production of exportable energy and waste heat. Obviously, the membrane process with gas permeation is very favorable with respect to exportable energy production, even more so since the waste heat consumption of a landfill very seldom exceeds more than 25 - 30 % of the energy of the biogas. The investment costs and profit calculations for this site was also compared to the plant with power generation by gas- or steam turbine. The simple membrane separation plant seemed clearly to be more attractive for landfills with a production of less than 1000 m^3(STP)/hr gas.

Teplyakov et al[41] has presented an interesting alternative of an integrated membrane system for biogas separation with moving liquid carriers. High purity of the methane gas is obtained in lab. scale experiments. Alternative methods with a combined biological method and hollow fiber membrane separation increase the methane concentration from 60% to 96 % [42]. This type of combined process has a significant potential for utilizing landfill gas as an alternative energy source.

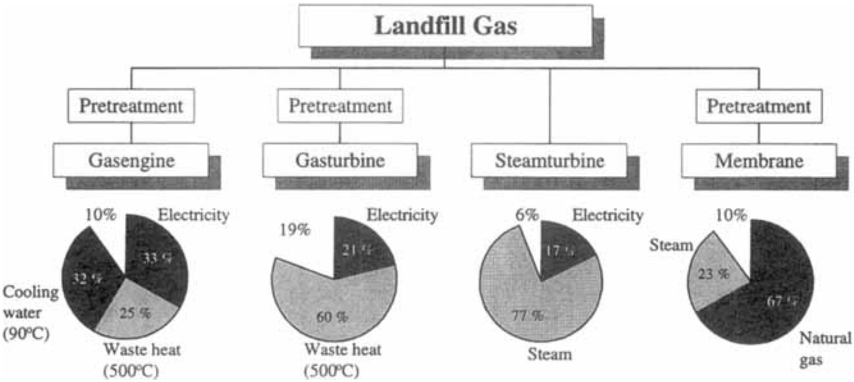

FIGURE 12 Illustration of energy balances for different processes utilizing landfill gas (Rautenbach [40], *reprinted from J. Membr. Sci.,* *87, p. 107, Copyright© (1994) with kind permission from Elsevier Science)*

The challenge is to prove the economy of the process in each case, and consider the environmental advantage of the process compared to energy produced from fossil fuels.

2.4 FUEL CELLS

2.4.1 Background

The direct conversion of chemical energy to electric energy has been a topic of investigation for scientists over the last two hundred years. In 1800 Volta constructed and experimented with the voltaic pile, which was the predecessor of modern batteries[43]. This was the first continuous source of electricity. The modern battery has been developed and improved ever since, and is still subject of intensive research.

In 1802, Gutherot performed experiments with two platinum electrodes immersed in water, and by sending direct current from a Volta primary battery he was able to split water into hydrogen and oxygen. By connecting the electrodes he made a current flow by recombining the gases to form water[44]. This was the first fuel cell ever made.

However, the principle of fuel cells is usually attributed to Sir William Grove who in 1839 connected six cells in series and applied sulfuric acid as the electrolyte[45].
A hundred years later, in 1940, several types of fuel cells had been tested, but none of them were good enough for practical applications. In the 1950s the US space research organization NASA showed great interest in fuel cells. A solid polymer fuel cell developed by the General Electric Company was chosen as the auxiliary power source in the Gemini space missions[46]. The power density of these cells was low (<50 mW/cm^2) and the use of unstable, sulfonated, cross-linked polystyrene ion-exchange membranes limited the cell life time[47]. The invention of the perfluorated sulfonic acid membrane Nafion® (DuPont) in 1962 meant that membranes with high chemical stability and thus prolonged lifetime was available. However, at this time there was very low interest in fuel cells. The energy crisis in 1973 gave an input to a large number of research and development programs, but it wasn't until the middle of the 1980s that the fuel cell research gained its renaissance.

2.4.2 Current Technology and Applications

In contrast to the practical difficulties in having a fuel cell work efficiently, the operating principle is very simple. The solid polymer fuel cell (SPFC) consists of two porous electrodes separated by a proton conducting membrane (see Figure 13[48]). The fuel is supplied to one electrode; air or oxygen to the other. The cell reactions and the direction for transport is illustrated in Figure 14[49]. Each proton moving across the membrane combines with oxygen at the cathode to form water molecules - one water molecule per two protons. Water generated at the cathode can also diffuse back across the membrane, and achieving water balance at each electrode is of critical importance. The membrane and electrodes are bonded together in membrane-electrode assemblies, and a whole series of membrane-electrode assemblies are used in a fuel stack. As long as fuel is supplied to the electrode, the fuel cell will generate electricity. This is in contrast to the battery which needs to be recharges regularly, which is also time-consuming.

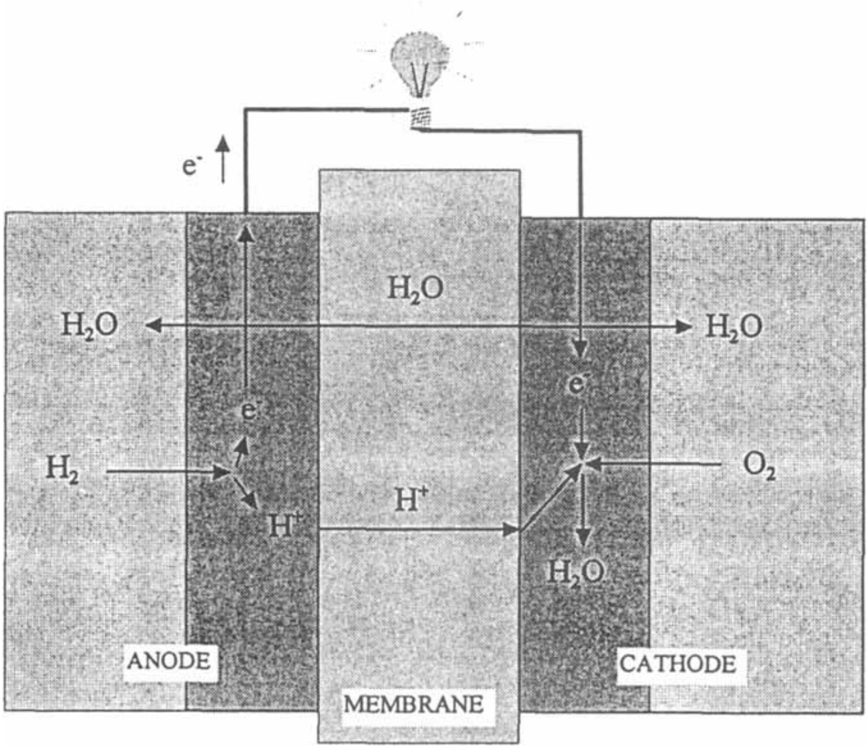

FIGURE 13 Illustration of the transport and reactions occurring in the solid polymer fuel cell (SPFC) during operation. Cell consists of two porous electrodes separated by a proton conducting membrane (Moeller-Holst [48])

Presently the phosphoric acid fuel cell is the most fully developed of the fuel cells, with a large number of demonstration units operating world-wide Then there are fuel cells based on molten carbonate and solid oxide (high temperature), but these have mainly been used for niche applications [50].

2.4.3 Novel Developments and Potential

Solid polymer fuel cells are considered to be the most promising for electric vehicles because of its simplicity and rapid start up. The properties such a cell should exhibit

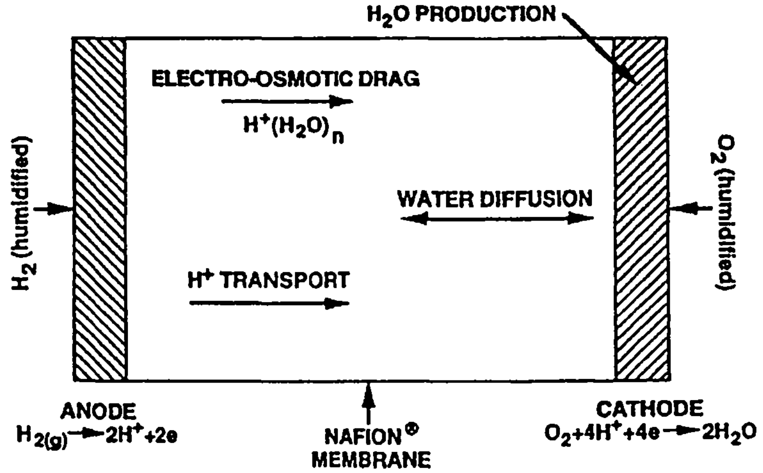

FIGURE 14 Illustration of the water transport and production occurring in the solid polymer fuel cell (SPFC) (Zawodzinski et al [49])

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is easy to write, but difficult to make in practice. The key requirement is high ionic conductivity; furthermore it should exhibit chemical and mechanical stability, low permeation rate for hydrogen and oxygen, and low electronic conductivity. The Nafion® membrane (DuPont) and a similar membrane introduced by Dow Chemicals Co. both display these properties. Regrettably, these membrane materials are still much too expensive for general use in fuel cells. The latest development that seems to be very promising is PFTE grafted membranes* with polystyrene and then sulphonated. The sulphonation must be carefully done in order not to loose conductivity.

Hydrogen is considered to be the best fuel for solid polymer fuel cells, however there is still a debate on how to supply this hydrogen: it may be liquefied, compressed or adsorbed on a compound like $LaNi_5$. At present the option with high pressure gas is preferred. Then there is the question of whether it should be stored on tanks or reformed at site. If reforming is chosen, then methanol is usually preferred as fuel.

It is still only a vision that the SPFC can work directly on methanol as fuel. Energy produced by a fuel cell is very clean energy (as can be understood from Figures 13 and 14). However, the cost of energy to produce and supply the hydrogen either as liquefied, compressed or adsorbed fuel, must be considered in a total economical evaluation of competing technologies. The main advantage of fuel cells is that the environmental pollution aspect is moved from the sector of transportation(cars, buses, trucks..), to the hydrogen fuel production site where it can more easily be controlled. This will in practice have a major positive impact on the pollution generated by traffic which is a problem of great concern in big cities today. Westinghouse is one of the world's largest companies with expertise within power technology, and the company has committed themselves to deliver fuel cell modules for power generation (larger modules) by the year 2002. The prophecy is however that fuel cells will be available within the transport sector earlier than this due to the pressure on environmental considerations. Giants like Daimler-Benz/Ballard and Toyota have speeded up the work with their development. Höhlein et al [51] is reporting successful tests with an "on-board" reformer for automobiles, where hydrogen is produced from methanol and supplied to a proton-exchange membrane fuel cell.

3. CHEMICAL PROCESS INDUSTRY

The chemical processes included in this section are the petrochemical industry, electrochemical industry, pulp and paper, breweries and textile industry. Others will be mentioned under section 3.5 *Various Chemical Industries.*

3.1 CHEMICAL AND PETROCHEMICAL INDUSTRIES

3.1.1 Background

In the chemical and petrochemical industries there is a large potential for the use of membrane units wherever there is a need for separating reaction products or recovering valuable components. Only selected topics will be focused on here.

A major part of the industrial application covered in this current chapter involves gas separation. For these separations a dense (non-porous) membrane will usually be applied, and it is of great importance to understand the difference in using a *glassy** or a *rubbery** membrane for the applications.

Basically the transport of a gas, vapor or liquid through a dense, nonporous membrane can be described in terms of a solution-diffusion mechanism which means that the membrane will separate both on basis of molecular size and the component's solubility in the membrane material. The glassy, more rigid membrane will thus separate mainly on basis of molecular size, while for a rubbery membrane the component's solubility will be of greater importance. The nature of the components (polar, non-polar, condensability, ability to interact with the material etc.) will in any case influence the transport through the membrane and thus the separation of the gases. Hence the type of components and volume fractions in the gas stream to be processed, must be carefully considered for the choice of membrane material. Small amounts of nitrogen or air to be removed from a hydrocarbon gas stream will typically demand a glassy material in order to hold back the hydrocarbons, while a rubbery material will in general be used for the removal of small amounts of volatile organic compounds (VOC) from an air stream. It is very important for the process solution to focus on whether the permeate or the retentate will be the product stream. More than in many other types of membrane processes, it is important to have a fundamental understanding of the permeation process through the membrane in order to choose the right process solution. The dense membrane materials will typically be used for pervaporation processes and gas separations.

The selected topics focused on are:

a) recovery of hydrogen and production of syngas
b) dehydrogenation
c) separation of hydrocarbons
d) dehydration by pervaporation

In addition to the selected processes there is a large potential for the application of membranes for other types of separations like the recovery of alkanes and alkenes in a polymerization process, separation of isomers, upgrading of hydrocarbon waste stream for heat recovery etc.

The recovery of hydrogen and production of syngas and dehydrogenation (topics a) and b) are increasingly important in relation to the development of *catalytic membrane reactors* (CMR). The novel developments and applications of CMR are therefore covered in the discussion of these topics (section 3.1.3 b). Catalytically active membranes may in principle be combined with almost any chemical reaction to simultaneously increase product yield and/or separate products. The development is slowly progressing, and successful products for spesific chemical processes are continuously being reported (see section Novel Developments). The combination of a chemical reactor with a membrane separation is frequently employed to remove selectively one of the products of a mixture - such a system may also be referred to as a membrane reactor although the (catalyzed) reaction takes place in the bulk phase (gas or liquid) to be separated, and not on or in the membrane material itself. An example of this type is discussed in section 4.3, *Membrane bioreactors*.

A pervaporation process (d) is a membrane process in which the feed side is a liquid while the permeate side is a vapor as a result of applying a very low pressure downstream. This low (partial) vapor pressure downstream can be achieved by employing carrier gas or using a vacuum pump. For pervaporation, the main applications are dehydration of organic solvents and mixtures and removal of organics from aqueous stream. Pervaporation processes are thus covered in various sections of the article, like *3.1.2 and 3.1.3 c) separation of hydrocarbons, 3.4 Breweries* and *4.3 Removal of VOC from waste water streams.* A pervaporation membrane may in principle also be used as a catalytic membrane reactor, but this is not discussed here however. In section 3.1.2 only one important pervaporation process will be covered as an example; *the dehydration of ethanol.*

Dewatering of solid materials by application of microfiltration- (MF) and ultrafiltration-(UF) membranes is much used within chemical industries. The topic is not discussed separately in the current chapter, but is covered in relation to industries like *Pulp and Paper (3.3) and Waste Water Treatment (4).*

3.1.2 Current Applications

a) Recovery of Hydrogen and Production of Syngas

Membrane units for the recovery of hydrogen and production of syngas have been successfully implemented for some years in some chemical and petrochemical processes. This is especially true for the recovery of H_2 in refinery processes, ammonia production, and from methanol synthesis. The membrane units may thus have two purposes: to recover hydrogen and to adjust the syngas ratio in a process line.

Synthesis gas ("syngas") is a mixture of for instance hydrogen and carbon monoxide which have uses in both petrochemical and chemical processes (metallurgical and agri-production). Syngas is produced mainly from hydrocarbons by

- -steam reforming
- -partial oxidation of heavy oils
- -gasification of coke or coal

There is a significant variation in the required stoichometric ratio of H_2/CO in the various processes. For the benefits of these chemical syntheses it is desirable for the syngas to be introduced in the proper ratio, and processes which can adjust the ratio accordingly without sacrificing the hydrogen are thus attractive.

The commercial membrane units in use today are usually either based on a polysulphone hollow fiber* or a cellulose acetate spiral wound* module. The membrane unit then performs the bulk separation upstream giving the required H_2/CO ratio, or may de-bottleneck a process for the use of a cryogenic separator in the syngas production. Membranes compete with pressure swing adsorption (PSA) and cryogenic systems in these hydrogen recovery applications over a wide range of operating conditions, see Table IV[4]. Membrane systems have the advantage of low

TABLE IV

Comparison of the separations for the hydrogen recovery from refinery offgas (Scott, p.300)[4]

	Membrane Process		*Adsorption*	*Cryogenic*
	80^{0}C	120^{0}C		
Hydrogen recovery (%)	87	91	73	90
Recovery H_2 purity (%)	97	96	98	96
Product gas flow rate, 10^3m^3(STP)d or (10^6scfd)	70 (2.76)	82 (2.86)	64 (2.24)	82 (2.86)
Power (kW)	220	220	370	390
Steam (kg/h)	230	400	-	60
Cooling water (t/h)	38	38	64	79
Investments ($ millions)	1.12	0.91	2.30	2.66
Installation area, m^2 or (ft^2)	8 (86)	5 (52)	61 (651)	120 (1292)

capital cost and ease of operation, but competing systems usually deliver the purified hydrogen at almost the same pressure as the feed gas which results in lower compression costs than those of the membrane system where the hydrogen product is always ata pressure lower than the original feed.

An example of a flow diagram for the H_2 recovery in ammonia synthesis is shown in Figure 15[4]. Syngas mixed with air is converted to ammonia through steam reforming, and in this production the recovery of hydrogen is usually done by separation in a cryogenic unit for liquefying the ammonia. Since the equilibrium conversion rate of the ammonia synthesis is below 33%, recycling of non-converted products are essential. The figure shows a typical application of H_2 recovery by gas permeation from a bleed of an ammonia synthesis loop. The use of membranes is today an accepted alternative in this process.

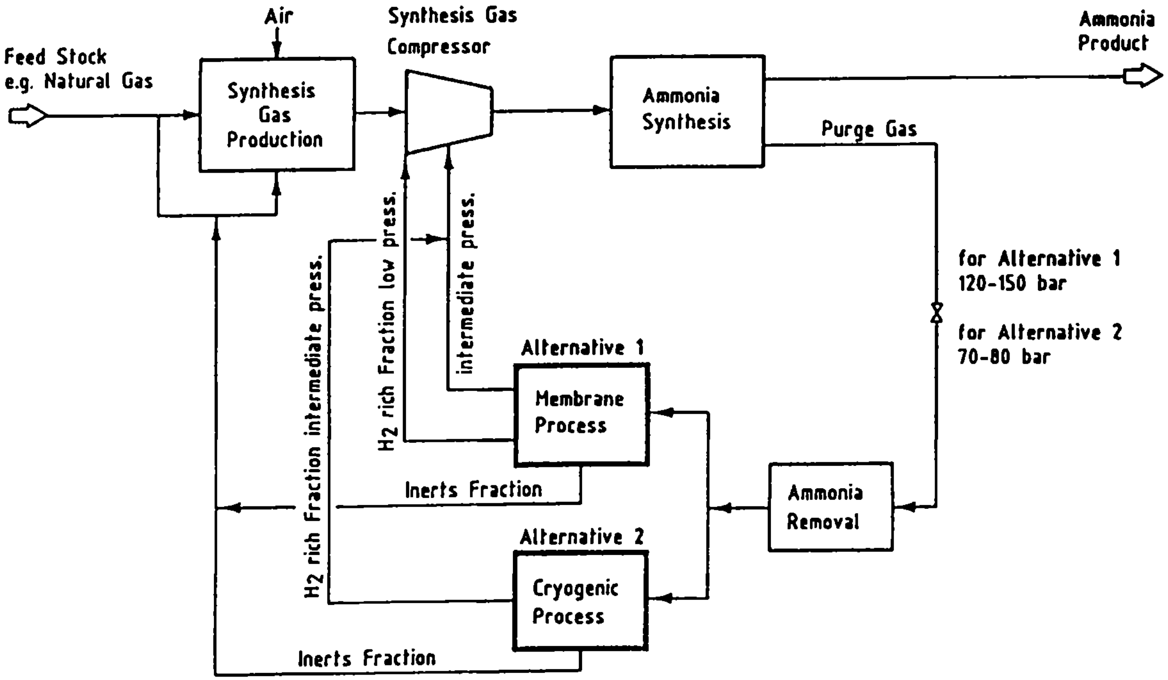


FIGURE 15 Simplified flowsheet of the ammonia synthesis with recovery of hydrogen either by 1) membrane process or 2) cryogenic process *(Reprinted from Scott*^{4}*, Handbook of Industrial Membranes, Copyright© (1995), p.293, with kind permission of Elsevier Science)*

b) Dehydrogenation

The latest development with membrane reactors indicate a very promising potential for *dehydrogenation* membranes coupled to refinery processes. This is discussed in the section "Novel Developments."

c) Membranes for the Separation of Hydrocarbons

The search for good polymeric materials capable of *separating hydrocarbons* on a large scale has not been very successful so far, but research has brought forward very interesting results, and a breakthrough for materials suitable for scale up may be expected soon (see section Novel Developments and Potential). Good polymeric membranes for hydrocarbon separation have been reported by Schuker and Ho at Exxon; but these have not yet been brought forward for commercialization.

The separation of hydrocarbons by liquid membranes has been studied in applications for the chemical and petrochemical industries, and suitable systems are recommended (Scott, section 13, Waste Water Treatment and Liquid Membranes)[4]. The systems utilize an oil-in-water-in-oil triple emulsion in which the aqueous phase is the membrane. Transport is by simple selective extraction and diffusion of one component into the aqueous membrane phase driven by a concentration gradient. The components to be separated are aromatics from hydrocarbons. The liquid membrane systems are not suitable for large industrial applications, but may be suitable for waste water treatment.

d) Dehydration of Ethanol - an Example of a Pervaporation Process

The principle of dehydration by membrane pervaporation is general and may be applied to various systems like dehydration of isopropanol, ethylacetate, ketones and other organic solvents. Here the dehydration of ethanol is given as an example. It should however be noted that dehydration of ethanol by 2-stage disitillation followed by molecular sieve dehydration is still the process of choice in many countries. Ethanol production is either based on fermentation or synthesized by direct catalytic hydration (of ethene) or such as in the sulfuric acid process. The fermented ethanol is a product of typically around 8-12% by volume which is concentrated mainly by distillation, and may then end up close to the azeotropic mixture (96%). Azeotropic distillation is an expensive procedure and the added dehydration agents are environmentally of concern. Use of membranes and pervaporation technology offers an excellent alternative to the traditional separation procedure for dehydration of ethanol. The permeate will consist mainly of water and a small amount of ethanol; the product will be 99.5% (or even higher) in ethanol. There are quite a few suitable materials available for the pervaporation membrane; and recommendations can easily be found for a material in the relevant concentration range [52]. The installation of pervaporation plants has slowly increased over the last ten years, and the units are of varying capacity.

Example: A schematic flowsheet of a pervaporation plant for ethanol recovery is illustrated in Figure 16. One of the largest plants for dehydration of ethanol is found in Betheniville in France, using polyvinylacetate (PVA) membranes (permeation area around 2400m^2) and producing 150,000 dm^3 per day of anhydrous ethanol.

Depending on product requirements and plant size it is common to optimize the pervaporation system by applying high flux, lower-selectivity membranes early in the train, followed by high-selectivity, lower flux membrane modules at the end[52].

Integrated systems are also often chosen with a combination of distillation / pervaporation and desulphation unit when needed.

A recent publication by Tsuyumoto et al[53] reports very promising results using a new type of hollow -fiber membrane for the dehydration of ethanol. The base material used was a polyacrylonitrile (PAN-B5) and through various techniques hydrolyzed and complexed uniformly so that a dense active layer was formed on the inner side of the membrane.

3.1.3 Novel Developments and Potential

There are two main ways the membrane units may be part of the industrial process for *recovery of hydrogen, production of syngas or dehydrogenation:* 1) a polymeric membrane performs the gas-separation of the components without interacting. This

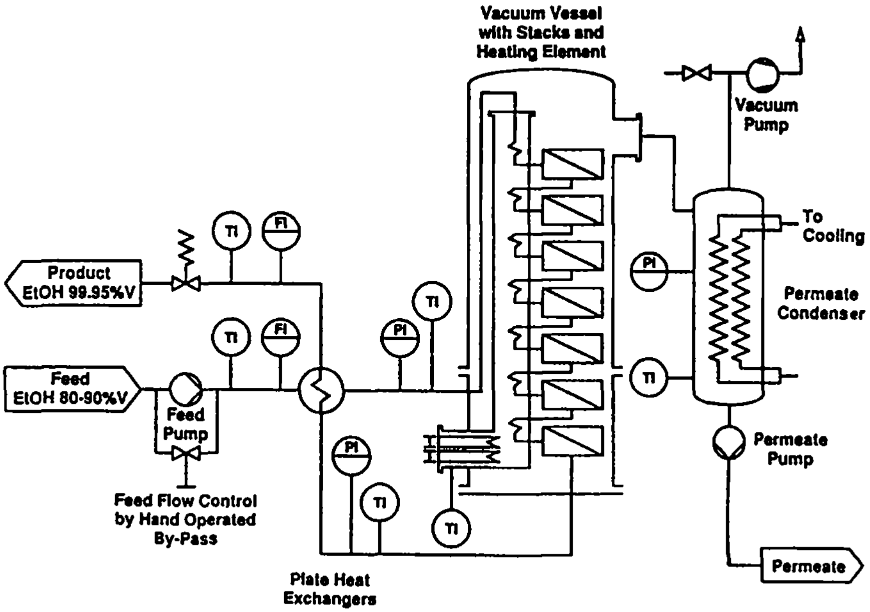


FIGURE 16 An example of a membrane pervaporation plant for ethanol recovery (Fleming and Slater [52])

would mainly be used for recovery of hydrogen and syngas ratio adjustment, while 2) a *catalytic* membrane initiates a reaction with the feed components and separates the reaction products (hence we have a dehydrogenation)

Another problem often addressed by petrochemical industry is *the separation of hydrocarbons from inert gases* (*N_2*) *or air, and separation of the hydrocarbon components.* The latter is very difficult, while there are suitable materials available for the first type of separation (see " *Current Applications* " in this chapter, and *chapters 2 and 5*).

a) Recovery of Hydrogen and Production of Syngas

-with Non-Catalytic Membranes

For the recovery of hydrogen with non-catalytic membranes the trend is that membrane materials are modified with carriers (fixed site) or surface treatment with various techniques in order to increase selectivity. There is a very large research activity that is focusing on these membranes for various processes. The carriers have to be selective for given components. This underlines the fact that a successful membrane solution should always be tailored for the specific process.

Large scale membrane modules using a selective surface flow (SSF) for dehydrogenation enrichment have recently been commercialized. An SSF membrane may consist of a thin layer of nanoporous carbon in a tubular form using macroporous alumina support. The dehydrogenation is one of the many promising new applications for the nanoporous carbon membranes. SSF membranes were tested by Anand et al [54], and the results reported show very high rejections for C_1-C_3 hydrocarbons (saturated and unsaturated) and CO_2 compared to H_2 with this SSF membrane. For comparison, a poly-trimethylsilylpropyne (PTMSP) membrane was also tested for the same systems. The SSF membrane is reported to exhibit much higher hydrogen recovery and hydrocarbon rejections than the PTMSP membrane under identical conditions.

A patent filed by Ube Industries Ltd. [55] describes the use of a polyimide membrane for hydrogen recovery in olefin polymerisation.

A hydrogen permeable metal membrane for high temperature gas separation is reported by Edlund et al [56] as having great potential for large scale applications. They claim their composite membrane exhibits improvements over previously developed metal membranes that include 1) stable hydrogen flux at 700^{0}C, 2) low cost and 3) chemical compatibility with many common feed-stream impurities (including hydrogen sulfide). A composite membrane of this kind may thus enhance the reaction of desulfurization for components like SO_2 and H_2S by using the right catalyst. The concept may as well be applied for other reactions like removal of NOx. (For the removal of H_2S, see separate section under 2.1.2.)

b) Dehydrogenation and Production of Syngas
- with Catalytic Membrane Reactors (CMR)

A membrane reactor may be understood as a membrane system emplying a catalyst to enhance the kinetics of a chemical process. The membrane may have the catalyst applied as a toplayer of the material, implanted in the membrane itself or filled into the bore of the tubular membrane (see Figure 17)[7]. The research is moving quickly forward for applications of the membrane reactors which are especially suitable for dehydrogenation, hydrogenation and oxidation processes. A membrane reactor may also be understood as a reactor vessel combined with a membrane (pervaporation) unit (see example in section 4.3 on Membrane Bioreactors).

The development of catalytic membrane reactors for the production of hydrogen and syngas has moved quickly forward over the last few years, and commercial units for general use may be expected within the near future. Steam reforming of light hydrocarbons is a key step for producing hydrogen and syngas. The focus is therefore continuously on development of improved catalyst performance and improved reactor tube materials A comprehensive review which summarizes the different catalytic options for this production is given by Pena et al (1996)[57]. In here, various processes, issues and practical difficulties are discussed, and it is emphasized that part of the ongoing research is still at an exploratory stage, while other parts of the technology is close to commercialization. The new emerging processes based on partial oxidation features are especially promising for syngas generation.

Possible applications of integrated catalytic membranes in petrochemical industry are:

- alkane dehydrogenation to olefins
- steam reforming of methane
- partial oxidation of methane

The catalytic membrane reactors (CMR) have been studied over the last years because they, in the context of chemical and petrochemical synthesis, offer interesting prospects for facilitating the production. CMR posseses the ability of performing two major tasks simultaneously in one single stage: carry out a chemical reaction and remove products. The ceramic and metallic composite membranes exhibit in general excellent thermochemical stability, although certain gaseous environments may be too aggressive and degrade the membrane [58]. A fairly comprehensive study discussing the influence of the operating conditions in a

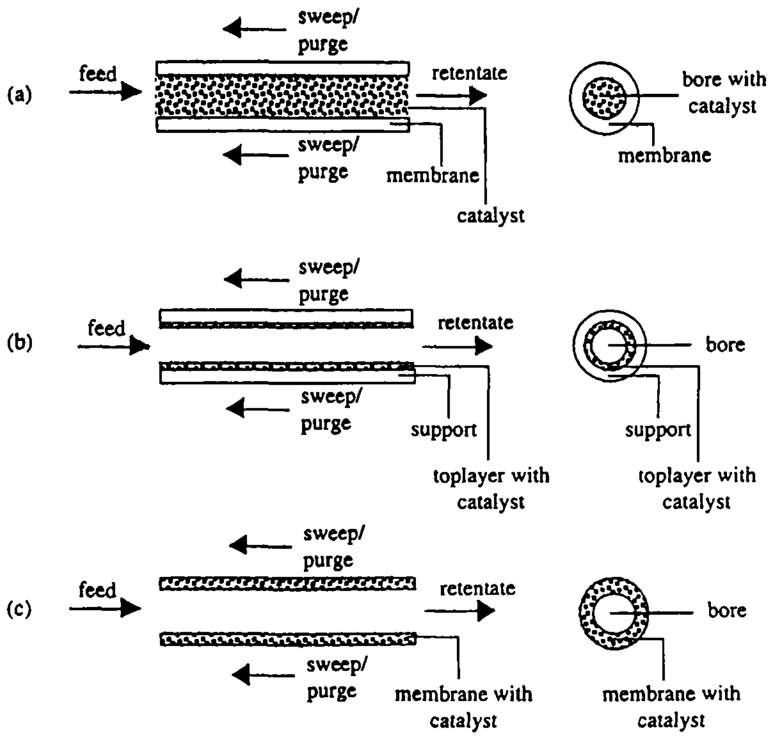


FIGURE 17 Schematic drawing of various membrane reactor concepts for a tubular configuration: (a) bore of the tube filled with catalyst, (b) toplayer with catalyst and (c) membrane wall with catalyst (*Reprinted from Mulder*[7]*, Basic Principles of Membrane Technology, 2nd ed., Copyright© (1996), p.395 with kind permission of Kluwer Academic Publishers)*

membrane reactor related to the water gas shift reaction is published by Basile et al[59]. This gives a good insight in the complexity of the CMR-system where both a reaction and separation will take place.

In Figure 17a[7] a membrane reactor with catalyst filled in the bore is illustrated. The figure shows the reacting gas components being fed into the inner reactor tube containing catalytic material which initiates the chemical reaction. As the reaction proceeds, the concentration of the products increases and because the membrane is selectively permeable to the products, these are transported across the membrane into the shell side. The products may then be swept by an appropriate carrier gas thus lowering the partial pressure of hydrogen .

Thin film deposition techniques have now made it possible to produce composite membranes with glass, ceramics or metals as a support. The catalyst may be Pd, Ni or V-Mg-O based [60,61]. Pd and Pd alloys are reported as most promising

Guy (1992)[60] is reporting results for three interesting applications: propane dehydrogenation, cyclohexanic naphtene dehydrogenation and natural gas steam reforming. For these chemical reactions, palladium based membranes show the best performance in terms of temperature resistance, hydrogen selectivity and permeability. One of the examples reported in the article, the dehydrogenation of propane on an industrial scale with a propene production of 100 000 tons/year, the necessary membrane area in the case of a dense palladium membrane would, according to their lab. results, be reasonable in the range of 50 - 312 m^2. The membrane thickness is however crucial for the flux and reactor performance and today there are still difficulties in preparing these membranes on a large scale .

Successful tests have also been performed for catalytic dehydrogenation of ethanol in a metal-modified alumina membrane reactor[62]. For the best performance, the membrane was modified with palladium or platinum.

Another process of special interest is the possibility of using a membrane reactor for the methanol synthesis - interesting results are reported by Struis et al (1996)[63]. The membrane used was a perfluorinated cation exchange material (Li-Nafion) combined with a commercially available catalyst bed operating on CO_2 and H_2 at 200^0C. There is still a way to go for commercialization though.

A recent review article on status concerning the natural gas conversion related to catalytic membrane reactors, Burch and Tsang (1997)[64] concludes that advances in this area will now require a much higher level of innovation in order to move the CMRs from the laboratories into pilot scale and then further to industrial scale.

c) Membranes for Separation of Hydrocarbons

Separations involving the removal of volatile organic compounds (VOC) are discussed under the sections "Water treatment" and "Gas Purification"

The petrochemical industry is in great need of improved separation techniques for alkanes/alkenes or higher hydrocarbons. Traditional separation operations like distillation or compression / liquefaction are complicated and expensive, and quite often a fairly large portion of the raw material is lost to flare. This is not acceptable in the long run for economical and environmental reasons.

Various types of membrane materials and modifications are reported for the separation of hydrocarbons. It will be a large step forward when suitable membranes are developed for this purpose. When a higher conversion of alkanes to alkenes is desired, then there is a large potential for the implementation of membrane reactors for this application.

For the separation of lower hydrocarbons in general some promising results were reported by Ilinitch et al in '92[65] using polyphenyleneoxide-based (PPO) copolymers, but the development of sophisticated surface treated membranes, membranes with fixed carriers, ceramic membranes and catalytic membrane reactors over the last years have clearly pointed the directions for this challenging separation.

Bakker et al (1996)[66] reported permeation data using a metal supported silicate-1 zeolite membrane over a broad temperature and pressure range for hydrogen, carbon dioxide and various hydrocarbons. In many cases the separation selectivity of a mixture does not reflect the one-component permeation ratio. Besides molecular sieving and difference in diffusivity, difference in adsorption is clearly the key factor in separation selectivity. Some typical separation selectivities obtained were:

Gas pair	*Temp.*	*Δp feed - permeate*	*selectivity*
hydrogen/n-butane	295 K	95kPa - 5kPa	125
n-butane/i-butane	295K	50kPa - 5kPa	27
methane/i-octane	423 K	25kPa - 5kPa	> 300

An inversion in separation selectivity is observed during a temperature programmed permeation which is explained from the temperature dependence of absorption. The silicate-1-zeolite membrane appears to be very stable upon thermal cycling and the permeation characteristics had changed less than 10% over a test period of 1.5 years. Depending on the volume of the gas stream and hence necessary permeation area, this membrane is clearly interesting for commercial applications.

Van Zyl et al[67] have been studying a very different material; a silver impregnated perfluorosulfonated ionomer membrane (Nafion®). They were mainly looking at the separation of alkanes / alkenes. The experiments were carried out with perfluorosulfonate ionomer membranes; well suited for the separation of petrochemical mixtures. The use of Ag/Nafion® membranes for separation of alkanes / alkenes have been reported by several[68] to prove efficient in small scale tests. Commercial membranes are available, but there is more evaluation needed before good membranes are available on a large scale for industrial use.

A very comprehensive screening of materials for the separation of hydrocarbons from methane has been reported by Schultz and Peinemann (1996)[69]. Forty materials have been tested, and the most promising two were found to be a modified polyoctylmethylsiloxane (POMS), a so called POMS-SSM (sub-surface membrane) and polytrimethylsilylpropyne (PTMSP). These two materials were then compared to the standard material, polydimethylsiloxane (PDMS). The transport properties were investigated dependent on process parameters such as temperature, feed pressure and feed composition under mixed gas conditions. Selectivities above 12 were obtained at acceptable fluxes. The durability over time still needs to be documented, but the potential is promising for commercial units within a reasonable time.

An interesting project is reported by Bessarabov et al[70] in which were achieved efficient separation of ethane and ethene from a mixture by the use of a large-scale liquid membrane contactor. The contactor comprised of a composite flat-sheet membrane with a nonporous diffusional layer made from polyblock copolymer polydimethylsiloxane and polyphenylsilsesquioxane, and an aqueous solution of silver nitrate flowing along turbulence promotor spacers between the membranes. The system seems to be sensitive to variations in process conditions.

3.2 ELECTROCHEMICAL INDUSTRY

3.2.1 Chlor-Alkali Industry

3.2.1.1 Background

In electrochemical processes it is usually necessary to separate the products at the anode and cathode with a porous diaphragm or membrane. In the chlor-alkali industry, the oldest type of electrolysis cell was a cell using mercury for cathode and no diaphragm was needed for separation of the chlorine and caustic. These old mercury type cells are, for obvious environmental reasons, now outlawed in most countries. They are now being replaced with either diaphragm or membrane cells. The diaphragm technology has, over the last decade, been facing big competition from ion-exchange membrane cells with driving force from a electrical potential gradient, and the membrane process is expected to be dominant in the chlor-alkaline industry by the end of the 20th century.

In Table V advantages and disadvantages of the three processes are listed. The table is also showing the global breakdown of chlorine production capacity by cell type (in 1994 for a production of 43 million tones). The remaining 2% of production not listed is, among other methods, done by electrolysis of HCl.

3.2.1.2 Current Applications and Novel Developments

In the membrane process, the anolyte and catholyte are separated by a cation-exchange membrane that selectively transmits sodium ions but suppresses the migration of hydroxyl ions from the catholyte into the anolyte. The process was started in early 1970s with the development of the perfluorosulfonate membrane, Nafion, by DuPont. The advantages of the membrane process are its energy

TABLE V

Advantages and disadvantages of the three chlor-alkali processes [71]

Process	Global[72] breakdown	Advantages	Disadvantages
Diaphragm process	43%	use of well brine, low electrical energy consumption	use of asbestos, high steam consumption for caustic concentration in expensive multistage evaporators, low purity caustic, low chlorine quality, cell sensitivity to pressure variations
Mercury process	35%	50% caustic direct from cell, high purity chlorine and hydrogen, simple brine purification	use of mercury, use of solid salt, expensive cell operation, costly environmental protection, large floor space
Membrane process	20%	low total energy consumption, low capital investment, inexpensive cell operation, high-purity caustic, insensitivity to cell load variations and shut-downs, further improvements expected	use of solid salt, high purity brine, high oxygen content in chlorine, cost of membranes

efficiency and its ability to produce , with no effect on the environment, a strong caustic of high quality[71].

The principle of the membrane ion-exchange cell is illustrated in Figure 18[71]. Saturated brine is fed into the anode compartment, where chlorine gas is evolved at the anode (comprising a titanium substrate with a thin coating of ruthenium oxide) and sodium ions migrate into the catholyte through the membrane. At the cathode hydrogen gas and hydroxide is generated from water . In the membrane cell this hydroxide combines with the sodium ion transferred through the membrane to give the product, sodium hydroxide. The cation exchange membrane allows the transport of Na^+ ions into the catholyte with the exclusion of Cl^- ions and represents, in principle, the ultimate separator for the chlor alkali industry.

Operating conditions in electrolysis involves extremes of pH and/or organic solvents and the materials that will withstand these conditions are very limited. For chlor-alkali cells the choice is restricted to perfluoronated carbon polymers (i.e. PTFE) with cationic exchange groups; sulfonic on the anodic side and carboxylic on the cathodic side, or certain ceramics (TiO_2, ZrO_2). The main properties required of the ion-exchange membrane (IEM) are (Scott, section 18)[4]:

1. Low electrical resistance. The permeability for the counter-ions under the driving force of an electrolytic potential gradient should be high to minimize the membrane IR loss.
2. High permselectivity. IEM should be highly permeable for counter-ions, but should be highly impermeable to co-ions, and to non-ionized molecules and solvents.
3. Good mechanical stability. IEM should be mechanically strong to prevent high degrees of swelling or shrinking due to osmotic effects when transferred from concentrated to diluted salt solutions
4. Good chemical stability. IEM should be stable over a wide pH range and in the presence of oxidizing agents
5. Good operating characteristics. Capable of operation over a wide range of current densities and under varying conditions of temperature, current density, pH.

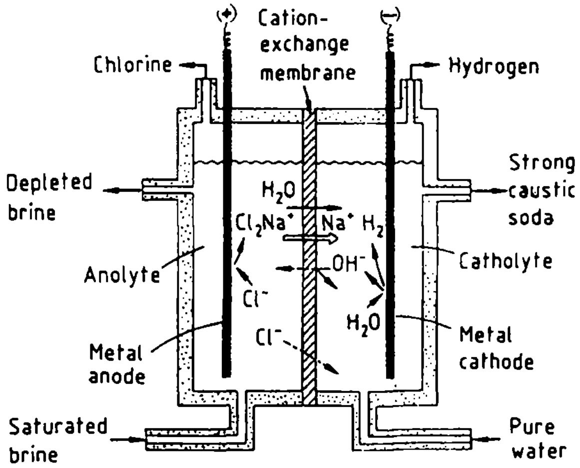


FIGURE 18 The principle of a membrane ion-exchange cell: transfer and transformed materials (Gerhartz [71])

The stability of the membrane material is very important since the cost of membrane material is high. They are expected to operate over a period of several years.
In order to meet all the requirements listed for the membrane above, the membranes are made as a bipolar type where the cathode of a cell is connected to the anode of the adjacent cell and so on in series, resulting in an electrolyses with small current and high voltage. The bipolar membrane is advantageous for attaining the minimum voltage drop between the cells. Several producers are on the market today with patented bipolar membrane cells[71] (ex. ACI, PPG, Tokuyama Soda, Hoechst-Uhde, Kvaerner Chemetics).

Examples of plants in operation today:

The ion exchange membrane (IEM) process is successfully operating today at Elf Atochem's chlor-alkali plants in USA and France[73], while Dow Chemical already has one in operation in Germany and is currently upgrading their Canadien plant for membrane technology: This is typically the technology choice for future investments for chlor-alkali producers all over the world today.

3.2.2 Magnesium Production

3.2.2.1 Background

Magnesium is produced commercially by electrolysis of magnesium chloride melts, involving two major steps: 1) preparation of the magnesium chloride feed and 2) electrolysis. The dehydrated magnesium chloride is fed to the electrolysis cells; Mg(s) is produced at the cathode and Cl_2 (g) at the anode. For each step of the process there are alternative ways, such as for the preparation of the magnesium chloride to the cell and the dehydration of the $MgCl_2$. The production of Mg is very energy consuming, and in addition to the complicated process itself there are toxic by-products to be removed in various purification steps.

3.2.2.2 Novel Developments and Potential

The process environment in the magnesium production is very aggressive; high temperatures and toxic gases. For this reason membrane technology solutions has not until recently been looked at as attractive for this industry. The challenges are big, but there are several places in the production line where membranes may be an interesting alternative, for instance for the purification of waste streams, for the production of $MgCl_2$ and for the purification of the chlorine gas coming from the electrolysis. Depending on the type of process downstream, the specified degree of purity for the gas and liquid streams will vary.

Example: Purification of chlorine gas; a process stream in the Mg-production

One of the most interesting process streams in the production line, is the purification of the chlorine gas coming from the electrolysis. This stream will carry traces of chlorinated hydrocarbons in addition to chlorine and air (around 10vol%; see simplified flowsheet in Figure 19). Two very different approaches are reported as

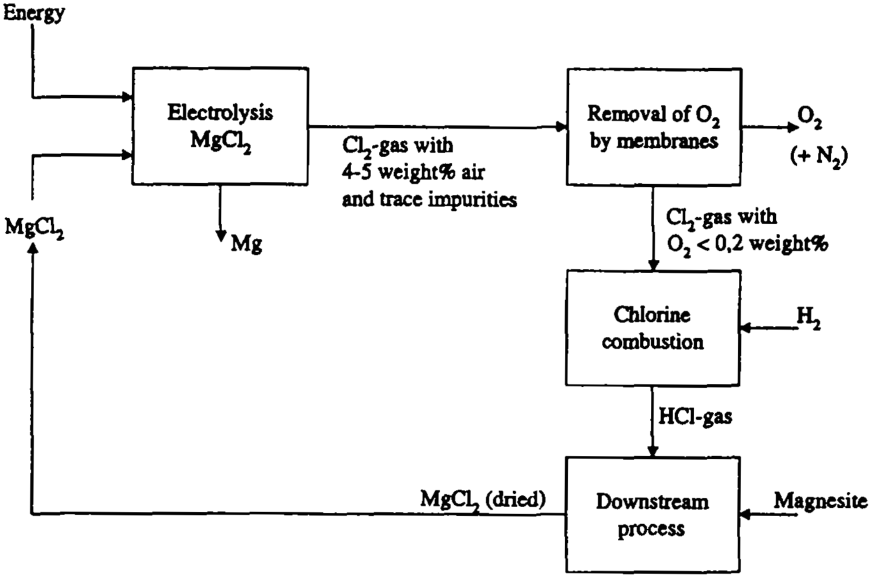


FIGURE 19 Simplified flowsheet for the magnesium production. Membrane separation is relevant for several steps in the production line (Hägg [75])

possible methods for the purification of the chlorine gas:

1) Pinnau et al (1995)[74] is suggesting a combined solution with compression and liquefaction of the major part of the Cl_2 before the membrane separation,

while 2) Hägg et al (1996)[75,76] is suggesting an integrated membrane solution without liquefaction or compression, and with process conditions mainly set by the feed gas stream coming from the electrolysis.

Both solutions suggest primarily a rubbery membrane where chlorine will be the permeating gas. The solution suggested by Pinnau is less demanding on the membrane and will probably be a good solution for removal of chlorine as an impurity in air streams or in gas streams where no toxic CHCs are present. The best solution for the purification of a concentrated chlorine stream from an electrolysis process, is usually to keep the temperature above 65°C to avoid precipitation of toxic CHCs (if present in the chlorine stream) in or before the membrane. The purification units for these compounds are usually (large) end-of-pipe solutions, and the company will usually prefer not to complicate the process (or add additional cost) by putting additional purification units within the process. The solution suggested by Hägg et al takes this into account - a few results are published[75,76].

The crucial question is, for all applications in such aggressive environments, the lifetime of the membrane material - the durability of the materials over time have to be documented. Combined solutions with the more stable perfluorinated materials are promising[77] - this is also discussed in section 5.3.

With the development of high-temperature, chemically stable membrane materials, the membrane technology will have a great impact on the renewal of the electrochemical process industry.

Effluent liquid streams from the electrochemical industry are often carrying (heavy) metal ions which need to be removed. This is often done by the use of microfiltration units Other solutions for the treatment of effluent streams in this industry may be by electrodialysis or the use of bipolar membranes - the concentration of the ions are then crucial for the application. Commercial membranes are available. (For a closer discussion; see section 4 on *"Waste Water Treatment").*

3.3 PULP AND PAPER

3.3.1 Background

During the last decade the paper industry has focused a great deal of attention on trying to reduce fresh water consumption in the mills. Recycling of water has become a must, but complete recycling without treatment or only partial purge is not feasible because of the accumulation of harmful dissolved materials inside the plant. This may lead to pitch problems in the paper machine and dark specks on paper. It is obvious that for recycling and reuse of water the potential for including membrane separation processes is great. There are at least three potential membrane applications in the pulp and paper industry[78]:

1. Effluent treatment of mechanical pulp mills using ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) technology
2. Incremental kraft recovery and caustic soda production through electrolysis of weak black liquor
3. Production of bleaching chemicals using bipolar membrane electrodialysis

The theoretical background and operating principles for the various membrane processes can be found in several textbooks and will not be described here [3,4,7]. It is only for effluent treatment prior to discharge that the use of membranes are currently in use in the pulp and paper industry. This is discussed in the following sections. Fouling is usually a big problem for these applications. The reduction of fouling is therefore always in focus for improved separation properties. Fouling is discussed briefly in the following sections on Pulp and Paper, and more in detail in the sections 3.4 (Breweries) and 4 (Waste Water Treatment).

3.3.2 Current Applications

Membrane applications in the pulp and paper industries today are mainly aimed towards the challenge of discharge treatment of the mills. Recycling and closing of internal water loops are quite complicated, and there are few standard rules for process solution. Ultrafiltration (UF) and reverse osmosis (RO) membranes for the treatment of mechanical pulp mill effluents and for water reuse are especially in focus. However, these modules are getting increased competition from nanofiltration (NF) membranes which naturally will have a higher retention and still an acceptable flux - this is discussed more closely in the following section "Novel Developments". Special membrane modules suitable for the pulp and paper industry have been developed, and integrated solutions with various types of filtration are today in operation. The membrane filtration has proved to be an economical and energy saving solution when good engineering is applied for the process solution and cleaning operation routines. Especially in Canada and the Nordic countries membrane installations of various kinds are today in operation in the pulp and paper industry.

Fouling and process conditions such as temperature and pH are of major importance and must be adressed separately for each process solution.

The major constituents of mechanical pulp mill effluents are various suspended solids, wood resin, lignin fragments and hemicellulosis as well as smaller molecular weight components such as sodium sulfite and sulfate salts. The performance of the membranes are thus evaluated by determining the reduction of certain measurable parameters in the feed solution such as chemical oxygen demand (COD), total organic carbon (TOC), total solids (TS) lignin, etc. In general, the following removals are expected for white waters[79]:

- UF: 100% of TS, collodial and bacterial matter; 10-50% of COD; in principle non-removal of salts (<10%)
- NF: >95% of TOC; >65% COD (UF+NF > 80%); 20-50% sodium; removal of Cl and SiO2 depends on bounding to organic matter
- RO: > 95% COD and all salts

A main point to notice is that with UF-membranes the salts will go through with the water, while this is not so for the RO-membranes. The RO-membranes have smaller pores for added selectivity where only water goes through, and will therefore demand higher feed pressures (3.5 - 5.5 MPa or 500 - 800 psig). In the UF, NF and RO-systems, both the chemical nature of the membrane surface and the composition of the feed stream determine the permeability and selectivity characteristics of the membrane.

Studies done at Paprican Institute in Canada by Paleologou et al[78] document that an ultrafiltration membrane with a membrane flux of 140 l/h m^2 or higher and with low concentration of solids (about 1%), will be more economical than vapor recompression, evaporation and freeze crystallization. It is proposed that the effluents should first be pre-treated through an approach such as settling, screening and flotation to remove suspended solids then followed by reverse osmosis or ultrafiltration. The purified water will then be recycled back to the mill for reuse.

The earlier UF-modules are of the tubular type, while during the last decade, the cross-rotational filter (CR-filter) has become increasingly popular due to a more compact module and high flux. The CR-filters were mainly adapted for the treatment of bleaching effluents and white water as well as concentration of coating color from wash water[79]. The CR filter (see Figure 20 for illustration) was developed by Raisio Flootek & Engineering around 1990. It can be installed alone or in a series with NF / RO units. A combination of CR filter and NF/RO reduces fresh water consumtion and thus the effluent discharge considerably. The CR filter is made up of filter plates (UF-membranes) stacked on top of each other and with rotor blades in between (on feed side). With the help of a throughgoing shaft propelled by an electric motor, the rotors move the waste water at high speed parallell to the membrane surface. Due to high-shear forces and low pressure difference, only a thin layer of contaminants forms and the filter is virtually self-cleaning. The filtrate is removed from the adjunctant compartment[79]. There should be a prefiltration of the waste water stream before it is fed to the CR-filters, taking the particle size down to appr. 150 μm. A principle flowsheet for a combined UF- and NF-system is shown in Figure 21[79].

An alternative to the CR-filter is the vibratory shear enhanced process (VSEP) where the membrane leaf is moved in a vigorous vibratory motion tangential to the face of the membrane. The feed slurry moves at an almost leisure pace between parallel leaf elements. The shear waves induced by vibration of the membranes repels solids and foulants from the surface giving free access for liquid to the membrane pores. The commercial module for the VSEP consists of an array of parallel leaf membrane discs separated by gasket, and spun at high speed in a torsional oscillation. Unlike cross-flow filtration, almost 99% of the energy input is converted into shear at the membrane surface. A variety of materials can be used in ranges of pore sizes from RO and UF to typically MF- membranes (Scott, page 425)[4]. The principle of construction of the VSEP-module is illustrated in Figure 22[4].

3.3.3 Novel Developments and Potential

a) Effluent Discharge

The main effort of pulp and paper industry today is treatment of effluent streams in order to reuse water and recover valuable chemicals. Environmentally the aim is

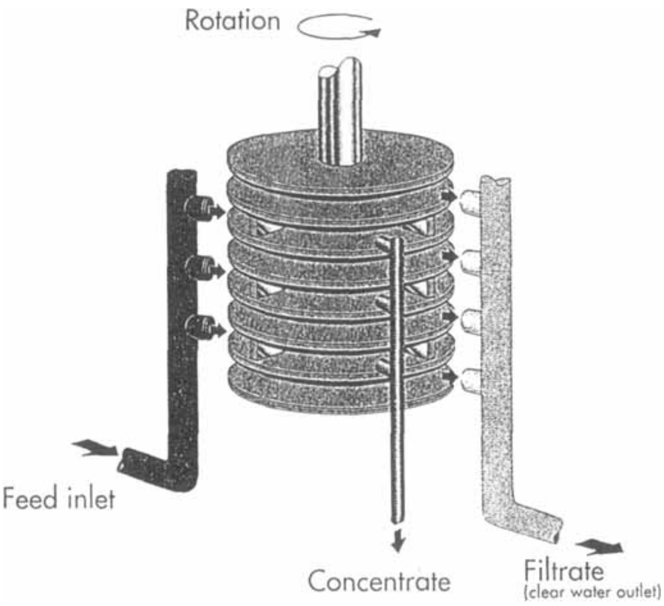


FIGURE 20 Membrane filter for application at pulp and paper mills. Illustration of the cross-rotational filter (CR) by Raiso Flootek Ltd [79]

effluent closed systems, and in order to reach this goal, membrane technology has a large potential. UF-membranes represent the majority of modules in use today, but nanofiltration (NF) membranes are receiving increased attention due to higher retention and still an acceptable flux. These two main type of separations with various types of membrane materials were tested out in the laboratory by Nuortila-Jokinen and Nyström[80] where it was found that in the nanofiltration the membrane structure and the feed pH affected the results the most, but on a whole, very good results were obtained in general by NF-membranes. Fouling was the main problem with UF-membranes. The possibility of pre-treatment with ultrafiltration before nanofiltration is also discussed, although better reduction with respect to parameters like TOC, COD and TS was obtained with NF when no pre-treatment was done.

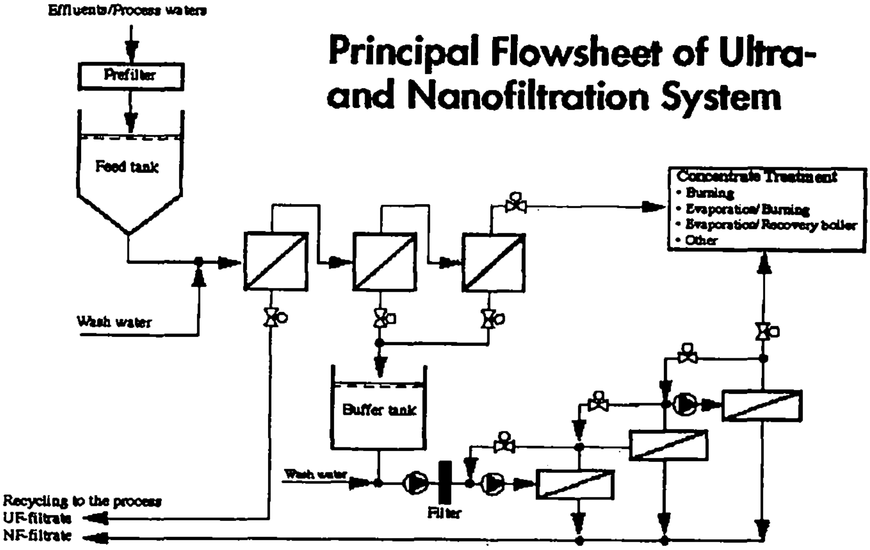


FIGURE 21 Principal flowsheet of combined ultrafiltration and nanofiltration units for waste water treatment at paper mills (Raisio[79])

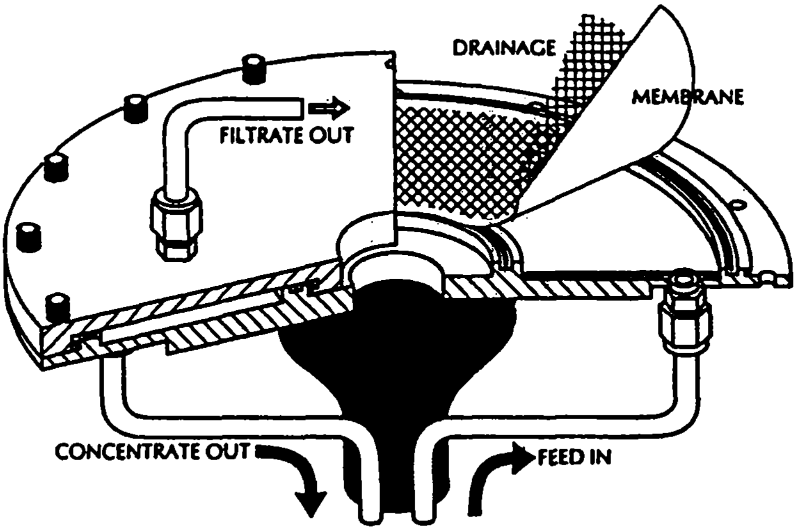


FIGURE 22 Membrane filter for application at pulp and paper mills. Schematic layout of the vibratory shear enhanced process (VSEP) filter

(Reprinted from Scott[4], Handbook of Industrial Membranes, Copyright© (1995), p.425, with kind permission of Elsevier Science)

In another study reported by Manttari et al[81] different membranes were tested for treatment of the effluent from a thermochemical pulp plant and a paper machine. The reduction in TOC, COD and TS were between 50 and 60% with UF-membranes and even better with NF-membranes (more than 80%). Chloride ions were not retained by either; these were however retained by RO-membranes, but for this purpose the RO-membranes had too low a permeability for industrial scale application.

The efficient use of UF- or NF-membranes to purify the effluent from paper mills and reuse the water has however been well documented. Thus these membrane units will, in the future, become a standard unit operation module. In each case the composition of the effluents must be carefully considered in order to use the right type. Rosa and dePihno[82] have evaluated four different types of UF and NF-membranes for effluent streams with organochlorinated matter and color for two different bleaching sequences. The highest removal of TOC and color achieved by ultrafiltration was 72 and 92 % respectively; while more than 90% removal of TOC and total removal of color was achieved with the nanofiltration membranes. Considering the development of membrane biofiltration, it is reasonable to believe that, in the future, these combined membrane processes will also find use in the purification of the effluent streams in pulp and paper industry. This is already implemented at some plants; for example at the Kirkniemi Mill in Finland where they are using both biological waste water treatment, ultrafiltration (CR) modules and nanofiltration in the waste water treatment.

The development of better module design, optimized module configuration and resistant membrane material is continuously ongoing to reduce fouling and wear due to tough process conditions. A novel method under investigation to reduce fouling is the use of ultrasonic fields to control the fouling by eliminating the gel layer. Experimental tests clearly show that flux will depend on the ultrasonic frequency and the output power [83]. The method is not yet sufficiently documented, but is found to be very interesting; and results are reported from applied tests both for pulp and paper effluent streams and oily waste water. Another technique described by Jonsson et al[84] is to reduce fouling by applying "backshocks" to the membrane.

Methods to reduce fouling are also discussed in the sections "Breweries" (3.4) and "Waste Water Treatment" (4).

b) Increased Caustic Soda Production

By using membrane electrolysis there is a great potential for increased caustic soda production from recovery of the weak black liquor in kraft mills. The chemical recovery system is often considered to be the bottleneck of the kraft pulping due to its high capital cost. In the conventional recovery system the sodium and sulfur are recovered as sodium carbonate and sodium sulfide and organics are burnt for steam generation. A recovery process based on electrolysis and a cation selective membrane will recover the sodium as sodium hydroxide.

An example of the integrated membrane process is shown in Figure 23[78]. The proposed solution will take a portion of the weak black liquor (WBL) into an electrolysis cell where pH is brought down to just before the precipitation of lignin, while at the same time high quality caustic soda is produced. As can be seen from the figure, this solution will reduce the size of the process stream going to the multiple effect evaporator. The main challenge is here, as in many industrial process streams, to document durability of the membrane over time.

c) Recovery of Chemicals

-by the use of Bipolar Membrane Electrodialysis (BME)

The consumption of chlorine in the pulp and paper industry is decreasing because of concern about the environmental effects the chlorinated compounds may have. As caustic soda production is currently linked to chlorine production and the demand for sodium hydroxide has remained high, there is a need to find cost-effective approaches for saving or producing caustic soda[78]. One such method is bipolar membrane electrodialysis (BME). Using this technology, chemicals used in bleaching such as caustic and an acid may be produced on-site from a process stream, a waste stream or

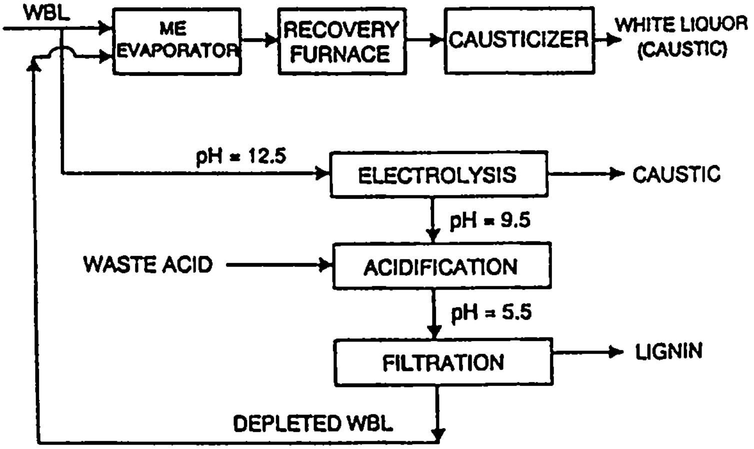


FIGURE 23 Simplified flowsheet for an integrated membrane process for a proposed incremental Kraft recovery process based on the electrolysis of weak black liquor (WBL = weak black liquor, ME Evap. = multiple effect evap.) (Paleologou [78])

from water soluble salts. This is schematically illustrated in Figure 24[78] If a salt solution such as sodium chlorate is fed between the first bipolar membrane and cation-selective membrane, then the positive ions will migrate towards the negative cathode and will "pick up" hydroxide ions produced from dissociation of water within the second bipolar membrane. Thus chemicals like NaOH and $HClO_3$ are recovered. The NaOH may go to bleaching and the $HClO_3$ to a modified chlorine dioxide generator. Several papers are presenting results from research within this field [85,86,87]; and discuss the use of two or three compartment configurations related to the product purity and current efficiency. The technology has a great potential for the pulp and paper industry, but still there seems to be a way to go before these bipolar membranes are proven technology. Thompson et al[85] has examined the economics of integrating BME into kraft mill operations for on-site productions of caustic and sulfuric acid from sodium sulfate; a by-product from chlorine dioxide generators The economics were analyzed for a base case in which the acid and base were both credited.

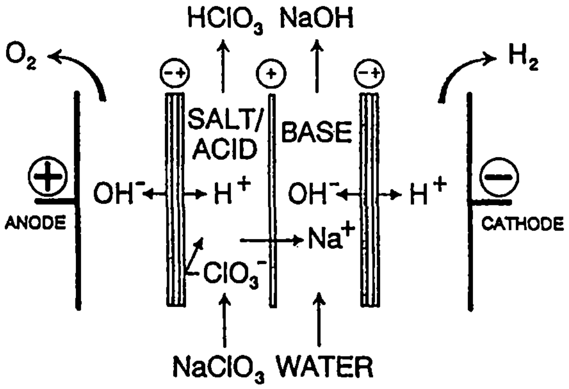


FIGURE 24 Illustration of a bipolar membrane electrodialysis unit cell for the generation of acid (chloric acid) and base (sodium hydroxide) from salt (sodium chlorate). (Paleologou [78])

However, the economics of a BME-solution will to a large degree depend on membrane lifetime and cost.

- by the use of Membrane Electrodialysis

In the kraft process black liquour is burnt to recover and reuse active pulping chemicals. Heavy loads of dust enriched in chloride and potasium are produced, and collected in electrostatic precipitators (ESP). The dust may then be dissolved in a diluted sulfate solution and feed it to a membrane electrodialysis unit for reuse and recovering of valuable components. The products from the electrodialysis process are a diluted (chlorine depleted sulfate/carbonate) solution which may be recycled back to the black liquor, and a concentrated aquous chloride solution which may be routed to waste water treatment or used in chlorine production for the bleach plant. Good documentation for the economical and efficient removal of chloride from dissolved dust coming from the electrostatic precipitator (ESP) in the kraft process, is given by Pfromm[88]. In the described process (see Figure 25) it is emphasized that no leaching

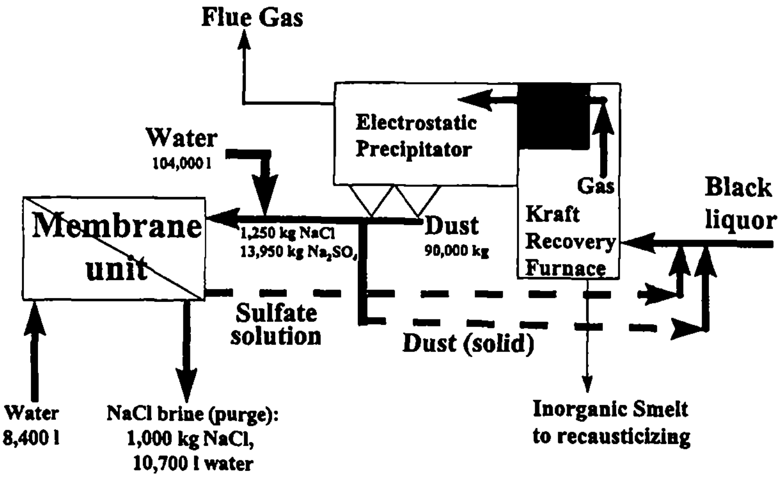


FIGURE 25 Example for application of electrodialysis to remove chloride from the Kraft process. Electrostatic precipitator dust is dissolved, dechlorinated and recycled to the process (basis: typical daily load of 1000 kg NaCl is removed)
(Pfromm[88], reprinted from Membr.Techn., 89, p.7, Copyright© (1997) with kind permission from Elsevier Science)

or pre-treatment of the ESP was needed for successful long-term chloride separation experiments with actual mill materials.

3.4 BREWERIES

3.4.1 Background

The brewing of beer has for generations been considered almost an art in the traditional breweries; handing down the recipes and production methods from father to son. The two main quality demands in all brewing before bottling are in any case to 1) preserve the organoleptic quality (taste) and 2) clarify the beer for storage. The ability of beer to withstand deleterious changes can be categorized into physical and chemical stability. Biological stability is impaired by the action of non-desirable microbiological growth after packaging, the exception being further fermentation and conditioning due to the inclusion of specific organisms may be desired for certain beer styles. Physical stability can be further categorized into flavor and colloidal stability i.e. the ability to withstand changes in aroma and palate and the resistance to deterioration in clarity[89].

Earlier the breweries traditionally used filtration with adsorptive depth media (such as asbestos and cellulose) and thermal pasteurization. Although depth filtration is still the most economical method for initial clarification, use of membrane filtration as the final step is continuously growing as it offers absolute removal of microbiological particulates without the use of chemicals or heat.

Fouling:

The major problem in application of membranes in breweries is fouling.

Fouling may be observed in membrane filtration as serious flux decline. The flux decline can be caused by several factors such as concentration polarization, adsorption, gel layer formation and plugging of the pores. All these factors induce additional resistance on the feed side to the transport across the membrane, and must be treated in different ways. Polarization is a reversible processes while the other phenomena mentioned may give permanent flux reduction. The various fouling phenomena will, in general, need different approaches for treatment.

Roughly three types of foulant can be distinguished (Mulder, chapter 7)[7]:

- organic precipitates (macromolecules, biological substances, etc.)
- inorganic precipitates (metal hydroxides, calcium salts etc.)
- particulates

Fouling is very complex and difficult to describe theoretically. Even for a given solution it will depend on physical and chemical parameters such as concentration, temperature, pH, ionic strength and specific interactions. However, for a good process design it is necessary to obtain reliable values for flux decline.

Extensive review articles have been written on fouling[90,91] for the interested reader.

Here the problem is also discussed in the sections on "Pulp and Paper" (3.3) and "Waste Water Treatment" (4).

3.4.2 Current Applications

The first use of polymeric microporous membranes for beer stabilization was reported early in the 1960s; and the beer was then sold as "cold filtered". Miller Brewing Co. promoted their cold filtered beer around mid 80's, when most breweries still were making their beer the traditional way. Today a growing number of companies all over the world report the use of membrane filters for stabilization in preference to pasteurization.

Microporous membranes provide the ability for guaranteed sterile filtrate; the micro-organisms are rejected. Type of membranes used are either ultrafiltration (UF) or microfiltration (MF) membranes; the pore sizes indicating what type of filtration is being used. (Typical pore sizes are; UF: 20 - 1000 Å and MF: 0.1 - 10 µm.) Typically a 0.65 µm pore size membrane will remove all yeast and significantly reduce bacterial loading indicating what type of filtration is being used.

Details on current applications for breweries can be found in the handbooks of Ho-Sirkar[92] and Scott[4]; details on theory for membrane filtration and fouling in Mulder[7].

3.4.3 Novel Developments and Potential

The use of membranes in breweries will increase as the problems of fouling and selective removal of certain components steadily find better solutions. The influence of the module design on flow pattern and thus efficiency of performance is also receiving increased attention.

The layer building up on the feed side of the membrane will mainly consist of carbohydrates and minerals, while the proteins will have a tendency to go into the membrane and block the pores. To solve the first problem various techniques are reported as successful, but the most efficient method seems to be the backpressure washing [93,94]. According to Gan et al[94] this will be especially effective if combined with staged increases in stage-membrane pressure. They report having achieved flux improvement of 400%. When the pores in the membrane filter are blocked, the regeneration of the membrane is more difficult. There are methods available to regenerate the filter, but more emphasis is being placed on using membranes with decreased affinity for proteins. This may be done by surface modifications or coating. A phospholipid coating on a polyvinylidene fluoride membrane is reported by Reuben et al[95] to be especially effective, while Shimada et al[96] reports a steady-state flux increased by 100% by using a surface modified glass membrane treated with two types of silane coupling agents. In membrane filtration of beer there will typically be protein-membrane interactions in the form of protein adsorption on the surface thus producing a protein-membrane "composite". This involves a build-up of a "secondary dynamic membrane". The mechanism of the flux decay for such a membrane has been studied by Blanpain et al[97] and they found that the actual mechanisms involved are related both to the internal and external fouling by the macrosolutes, thus a combination of different types of treatment will be necessary.

Low alcohol beer:

There is a considerable demand for the production of low alcohol beer, the objective being to supply two full bodied products: a low-alcohol beer (around 2% wt ethanol) and a "non-alcoholic" beer, (< 0.5% wt ethanol). This may be achieved in two ways; either by alteration of the brewing process to ferment less alcohol, or by the removal of ethanol by for example distillation, dialysis or reverse osmosis (RO). The distillation changes the taste of the beer and is very expensive. Dialysis results in a high percentage of small molecular weight components being lost in the permeate which gives a light bodied beer, but may also affect aroma and taste more than desirable. Other more selective membrane processes used in conjunction with dialysis may correct this. For the diafiltration a cellulose based material, cuprophane or polysulfone seem to be suitable[98].

The reverse osmosis (RO)-membranes have relatively low ethanol rejection compared to other constituents, see Table VI [4]. As can be seen from the table, the cellulose

TABLE VI

Composition of Feed and Permeate of Beer treated by different RO-membranes (Scott, page 760)[4]

Composition	*Cellulose Acetate*		*Thin Film Composite*	
	Feed	*Permeate*	*Feed*	*Permeate*
Acetaldehyde	1.1	0.9	1.2	0.3
n-Propanol	16.2	14.5	11.7	0.0
Ethyl acetate	41.0	40.4	26.0	1.0
Isobutanol	25.3	19.4	14.4	0.0
Amy alcohol	23.0	17.8	20.3	0.0
Isoamyl alcohol	82.9	66.2	42.8	0.4
Isoamylacetate	4.8	4.3	2.7	0.0
Diacetyl	0.02	0.01	0.02	0.0
2,3 Pentanedione	0.02	0.01	0.02	0.0
Ethanol	5.3	5.4	3.7	1.0

acetate rejection of ethanol is as low as 5% which results in a very low alcohol content beer, while the thin film composite membrane referred in the table can reject some 70 - 75% of the ethanol and almost all the volatiles in the stock beer, thus retaining the quality of the low-alcohol beer.

Membranes in Quality Control:

The ultrafiltration process of biotechnological processes such as brewing of beer, needs continuous monitoring of quality in various ways. One efficient method used today is based on the on-line combination of ultrafiltration and column liquid chromatography. With this system the sugars, alcohols and organic acids can be monitored, and depending on the application 3-5 analyses can be performed every hour[99]. Osmonic biosensors are also available for measuring alcohol content continuously[100].

One very new area into which membranes are finding use in industry for food and beverages is the on-line monitoring of quality by *taste sensors*. The most interesting sensor reported is a so-called multichanneled taste sensor which is able to "taste" foodstuffs such as beer, coffee, mineral water and vegetables. The sensor is composed of several kinds of lipid/polymer membranes for transforming information of taste substances into electric signals analyzed by a computer. The output shows different patterns for chemical substances which have different taste qualities like saltiness and sourness, sweet and bitter substances. Amino acids can be classified into several groups according to their tastes[101].

3.5 VARIOUS CHEMICAL INDUSTRIES

The use of membrane filtration in purification of or recycling of process water is in general facing the same kind of problems or challenges independent of the of industry; UF, MF, NF and RO-membranes have to deal with fouling , plugging or degradation etc. In this article this is more thoroughly described in the sections for "Pulp and Paper", "Breweries" and "Waste Water Treatment", but can also be related to the textile industry and china production. Hence only selected examples from these industries are discussed below. Wastewaters from the mining industry will usually require more complicated membrane solutions like electrodialysis processes combined with reverse osmosis or even biofiltration.

3.5.1 Textile Industries

Large volumes of water are used in the textile industry for many purposes including washing, scouring, dyeing, printing, bleaching and finishing of cloth. The wastewaters generated in these processes contain a wide range of contaminants including salts, dyestuffs, scouring agents, fatty acids, surfactants, oils, greases oxidizing and reducing agents. The temperature of the wastewaters may vary between 30-90^0 C and the pH between 4-12. Reverse osmosis (RO) membranes have been found to be very suitable for treating wastewaters from textile industries, and are installed several places and. The RO-modules prove to be economic feasible because they will reduce the volume of wastewaters generated and make it possible to recover valuable components such as dye stuffs. The units may also be used for recovering of thermal energy in the hot wastewater [102]. Oil and grease have been efficiently removed and poyvinylalcohols recovered after the scouring of woven textiles by the use of UF-membranes; other components depending of type and size by the use of MF and NF membranes.

Example: Before raw wool can be carded and spun into yarn, it has to be cleansed (or "scoured") of its natural impurities. This is normally carried out by means of an aqueous process using hot water together with small amounts of sodium carbonate an non-ionic detergent. The level of impurities in raw wool is relatively high, varying from about 35 to 65% and comprises wool grease, water soluble impurities, sand and dirt. The traditional method of cleansing the wool normally utilizes some 10 liters of fresh water per kg of raw material and produces a highly polluted effluent which must generally be treated before disposal. The effluent load as well as fresh water consumption can significantly be reduced by implementation of a process including membrane filtration units and reuse of water. This has been fully documented by Turpie et al[103] reporting the results from installing a membrane unit at a mill in South Africa. At the specific mill a hydrous zirconium (IV)oxide membrane was used for the purification of wash water and water from the biological degradation ponds. The zirconium oxide layer was deposited automatically on the porous stainless steel sintered support. The mill was able to reduce their fresh water consumption by approximately half.

The coloring of textiles produces harmful waste such as heavy metal components and other toxic substances, but the dyestuffs are also valuable components to be recovered. The heavy metal components need special attention, and the development of bipolar membranes (see description in sections 3.3.3 and 4.4) will be an attractive alternative also for the textile industry.

With reference to the speed at which the membrane bioreactors (see section 4.3) are developing, one might see a potential for even further reductions of water consumption in the textile industries as well, and aim at a "closed system" as the pulp and paper industry is doing.

3.5.2 Producers of China and Porcelain

For the production of china and porcelain very special and fine clay is needed. The clay is thus a very valuable raw material and must be recovered from the waste stream. The traditional way of recovering the clay is space consuming and chemically intensive involving coagulation, flocculation and sedimentation. Separation with microfiltration membranes is a well suited method for the recovery of production materials[104]. The MF-membranes will typically have poresizes around 0.2 μm and separation of larger particles than this will thus be guaranteed. A large Norwegian company producing china, Figgjo AS, has nearly eliminated the clay in the effluent by using membrane filtration. Annually they recover 35 tons of clay with the MF-plant, meaning a pay back time of 5 years based on savings in clay alone.

3.5.3 Mining Industry

The effluent stream from the mining industry may contain both ordinary salts and harmful metals, phenols or other toxic substances. According to this, the solution for purification of the streams will often be different from industries described previously. A process which uses *seeded precipitation and recycling with reverse osmosis* (SPARRO) is reported to be very successful for desalinating calcium sulfate scaling mine water, a type of mine service water encountered in gold mining. The novel feature of the new process included, among other things, a low linear slurry velocity in the membrane tubes and a low seed slurry concentration. Evaluation of the SPARRO process and its novel features over a five year period confirmed its technical viability for the application mentioned (service water in a gold mine)[105]. For other types of nonscaling mine water the conventional membrane desalination process of electrodialysis reversal (EDR) and tubular reverse osmosis (TRO) is used [106,107]. Both the SPARRO and EDR process are in operation around in the world. A TRO-process which is successfully operating in Leeds, UK, and is treating water from an open-cast mine for drinking purposes. The water is originally heavily polluted by manganese and iron, and with pesticides from surrounding farmland [108]. The same type of process is also successfully treating saline wastewater for zero discharge at the Debiensko coal mines in Poland [109].

Wastewater from the coke industry is extremely troublesome to the environment and must be treated on-site. The wastewater contains large amounts of phenol and its derivates as well as cyanides. A solution to this problem is reported to be found by Bodzek et al[110] . They suggest a biodegradation of these toxic substances by the use of immobilized enzyme membranes. They claim that the introduction of ultrafiltration with enzymatic membranes (made of polyacrylonitrile) as first stage of biological treatment makes it possible to remove from the wastewaters some amounts of phenols and cyanides and to eliminate the necessity of mixing them with municipal sewage before they are passed to the biological treatment plant.

4. WATER AND WASTEWATER TREATMENT

4.1 Background

The global water and wastewater treatment industries are the largest users of membrane technology today. Water treatment is a rapidly expanding business in all areas of the world, especially in developing regions like Southeast Asia, with demand rising continuously from both the domestic and industrial sectors. By the year 2000 it is predicted by the United Nations that Asia will consume about 75% of the fresh water totally produced.

An important question is then into which sectors is the fresh water consumed. Figures from Germany, which can be assumed typically for industrial nations, indicate that

69% of water consumption is used for thermal cooling applications such as power stations, 16% is service water supply for industrial use, 12% is for drinking water, and 3% is agriculture (Profile of the Intern. Membr. Industry, p.81)[1].

The main causes of water pollution are waste water from private households (most biodegradable substances like fats and proteins) and household chemicals (including chlorine compounds); industrial waste water with both biodegradable and non-biodegradable substances, heavy metals and carbon compounds; handling of oils and solvents from various industries.

Overall both waste water treatment regulations and drinking water standards are expected to be tightened. Together with the expanding clean water requirements by industry and emerging economic regions, the prospects for membrane technology are positive; especially the ultrafiltration membranes used in clarification and disinfection systems for drinking water and pre-treatment of industrial water and waste water, as well as the subsequent treatment with reverse osmosis and nanofiltration membranes. The very new membrane technology expected to be implemented on large scale in the future is the combined bioreactor-membrane filtration and the membrane contactors for degassing or removal of volatile organic compounds in water (VOC). These techniques are discussed below.

4.2 Current Application

As stated above, the standard membrane separations for water and sewage treatment are ultrafiltration, microfiltration and nanofiltration with varying types of material (polymeric or ceramic) and varying design of modules. Reverse osmosis (RO) modules have more recently come into consideration for water treatment in various ways - this is discussed in a separate section below. The basic principles for these membrane separations are excellently described in several textbooks; the reader is referred to the book of basic principles written by Mulder[7].

Membrane processes have received considerable attention for the separation and concentration of inorganics and organics from various wastewaters. The UF and MF processes are mainly concerned with removing solid particles, while the RO processes has become an attractive alternative for the treatment of dilute aqueous waste streams of various kinds since these RO-modules offer high fluxes and solute separations and can operate over a wide temperature and pH range. A good overview of current applications for wastewater treatment by these techniques (UF, MF and RO membrane separation) is given by Williams et al[111] and Scott[4]. In this article applications are also described under the sections on "Pulp and Paper", "Breweries" and "Various Chemical Industries" (3.3, 3.4, 3.5).

The list of producers for applicable modules for wastewater treatment is long, and it is in many ways a mature technology. The new membrane technology development within the field is focusing on how to improve existing modules and materials, how to reduce fouling (see also "Pulp and Paper" and "Breweries") and on how to remove hazardous components and biodegradable materials in the wastewater streams. Some of these aspects are discussed under "Novel developments and Potential".

Two fairly new technologies related to 1) the removal of VOC by degassing through a membrane contactor and 2) the bioreactor-membrane filtration are also described under section 4.3 ("Novel Developments").

The production of ultrapure water for the semiconductor and pharmaceutical industries is an application in use which deserves special attention. Electrodialysis or high performance RO membranes are combined with mixed-bed ion-exchange resins to produce completely deionized water. No chemical regeneration of the resin is necessary. Important parameters of the ultrapure water are conductivity, total organic carbon (TOC) and the number of particles and bacteria (see Table VII for specifications). Pretreatment may be necessary depending on the quality source of water, and a post-treatment involving ultraviolet sterilization, ion-exchange polishing and ultrafiltration to remove particles coming from the ion-exchange beds applied[7,112].

4.3 Novel Developments and Potential

a) Advances in UF, MF, NF, RO Technologies for (Waste)Water Treatment

Advances in the UF, MF and NF:

A wastewater stream will often contain oily compounds which easily build up a gel layer and thus reduce the water flux through the membrane. Hamza et al[113] has

TABLE VII

Specifications for Ultrapure Water (Mulder, p.482)[7]

Electrical resistance (MΩ.cm)	> 18
Number of particles (ml^{-1})	< 10
Bacteria count (ml^{-1})	< 0.01
Total organic carbon (TOC), (ppb)	< 20

developed a membrane with low surface energy to reduce fouling in UF-applications, and reports successful results from experiments with a surface modified polyethersulfone (PES) ultrafiltration membrane. The surface was modified with various amounts of macromolecules as additives, and it was found that a modified PES-membrane had superior performance reflected in their high flux when treating oil-in-water emulsion, than the control membrane (unmodified).

It is also interesting to notice the difference in permeate flux reported by Nakatsuka and Miyano[114] where a hydrophilic cellulose acetate (CA) membrane was compared a hydrophobic polyethersulfone (PES) membrane. The flux through the CA membrane was found to be much higher than that of the PES-membrane; a phenomenon which was explained by the difference in membrane fouling due to adsorption of substances in raw water on and in the pores of the membranes. In order to maintain the high and stable flux of the CA-membrane , the operating backwashing pressure would be more than twice as high as the filtration pressure. Efficient removal of organic compounds from raw water was accomplished by the fouled CA-membranes.

In general it can be stated that the MF- and NF membranes in wastewater treatment or public water supply will need some type of pretreatment of the water stream, while the UF-membranes can be modified in various ways for improvement of the membrane filtration. Successful experiments with the latter are reported by several authors[115,116,117] .

The quality of the raw water to be purified is always the crucial question for choosing the type of membrane, pore sizes and material. Ericsson and Trädgard[118] have investigated the purification of raw water from lake Muskan in Sweden which has a high color content of mainly humic substances and also taste and odor problems. They evaluated ceramic MF and UF membranes, polymeric UF and NF membranes with respect to the need of activated carbon treatment as well as for comparison of results from conventional water treatment.They found that the efficiency of added powdered activated carbon (6 mg/l) in the influent before membrane filtration was negligible. The removal of color and organic matter was almost complete with nanofiltration (NF), and activated carbon treatment of the permeate was required with the UF-menbranes. The drinking water quality was on a whole found to be better and more consistent with the NF-process, but that the costs are still higher than for the conventional treatment.

A "hybrid" process, actually a dual membrane process, may be the solution for water treatment rather than one single type of membrane process. A process of this type is presently in the early stage of commercialization by a US company. Their hybrid process is claimed to have significant advantages for the treatment of wastewater streams containing oily substances, halogenated organics or organic solvents (Scott, page 626)[4]. The first stage uses a cellulosic hollow fiber membrane and the permeate then passes to a separate NF or RO system. In some applications, the second stage permeate is further treated by activated carbon to remove trace organic elements. For the most difficult waste streams containing appreciable quantities of soluble hydrocarbons a four-stage process is advised comprising pretreatment prior to hollow fiber membrane separation, a further nanofiltration or reverse osmosis membrane stage, and final treatment with activated carbon to remove any remaining low molecular weight dissolved organics. Only the first two steps are required for waste streams which consists of only insoluble components, such as produced waters and PCB-contaminated wastewaters. It is reported that the modules have reduced PCB concentrations in water from as high as 132 ppm to less than 0.5 ppb. (Scott, p.627)[4]

A promising new centrifugal membrane module is being developed at the Univ. of Victoria, Canada[119] which utilizes a spinning centrifuge to reduce membrane fouling and concentration polarization. The research group claims that the method will result in higher flux, and expects the unit will find applications in various treatments of industrial waste and process waters.

Advances in the RO-technology:

The high level of nitrogen-compounds in wastewaters, domestic or industrial, may be very harmful to environment in certain sensitive areas. The removal of nitrogen today is largely based on chemical precipitation as it is also important to recover these valuable components. A combination of precipitation and RO-units is suggested by Bilstad[120] where the nitrogen is recovered as $(NH_4)_2(SO_4)$, NH_4NO_3 or $(NH_4)_3(PO_4)$. There seems however to be a better solution to the problem of nitrogen removal by using the new alternative technique with membrane bioreactors. These combined membrane modules are in the early stage of commercialization (see section b).

The very high levels of fluoride and sulfate often found in groundwater may also effectively be handled by the use of RO-units.

The Japanese membrane manufacturer, Nitto Denko Corp.[121], has developed a high-performance RO-membrane and claims it has an amazing salt rejection of the 99.7%. If these results can be reproduced over time, it may lead to the extension of ion-exchange resins often applied after the RO-units. Furthermore, they report that the membrane can operate effectively under ultra-low pressure conditions - down around 0.5 MPa.

The problem of fouling and operation of RO-units have been closely addressed by several authors, here only a couple of references will be mentioned:

Pervov et al [122] reports comprehensive studies and field testing, with RO-modules, and their main concept is based on the knowledge of foulant behavior during accumulation on the membrane surface. This has resulted in the development of a desalination technique and a specific RO-module for well water treatment and surface water treatment for tap water quality. Antiscalant addition is implemented automatically through the use of solenoid valves and injectors. The unit uses a small built-in antiscalant dosing system with built-in storage tank with a volume enough for 1.5 - 4 months operation.

b) Membrane Bioreactors

The combination of membrane separation technology and bioreactors has led to a new focus on wastewater treatment. The application of membranes has led to a very compact wastewater treatment systems with an excellent effluent quality. For concentrated wastewaters, like industrial streams and landfill leachate, the membrane bioreactor has already been successfully applied at some plants in full scale. A good overview of the state of art and potential is given by vanDijk and Roncken[123].

It should be pointed out that a bioreactor combined with membrane filtration and a membrane biofilter is not the same type of process. They are however both referred to as membrane bioreactors (MBR). The membrane biofiltration is a combined process, and is in principle a biological treatment process wherein membranes (UF) concentrate biomass, enhancing the effectiveness of the biological process, clarifies the bioreactor effluent and virtually eliminates the production of sludge. The effluents can be further processed, if required, with reverse osmosis or activated carbon (refer to Figure 26, illustration a). The membrane biofilter is usually understood as a bubbleless aeration (with oxygen) of the bioreactor through a hollow fiber. This is illustrated in b), Figure 26. The third type is the extractive MBR as shown in c) in the same figure. Here organic pollutants from hostile industrial wastewater are extracted through the membrane and transported into the bioreactor for degradation[124]. When a bioreactor is not an active part of the membrane treatment, it may be necessary to disinfect the membranes with respect to microorganisms on a regular basis. This can be done in several ways. One solution is suggested by Alasri et al[125] where they have been using a combination of peracetic acid and hydrogen peroxide, and they compare successful results to the more standard method of using chlorine

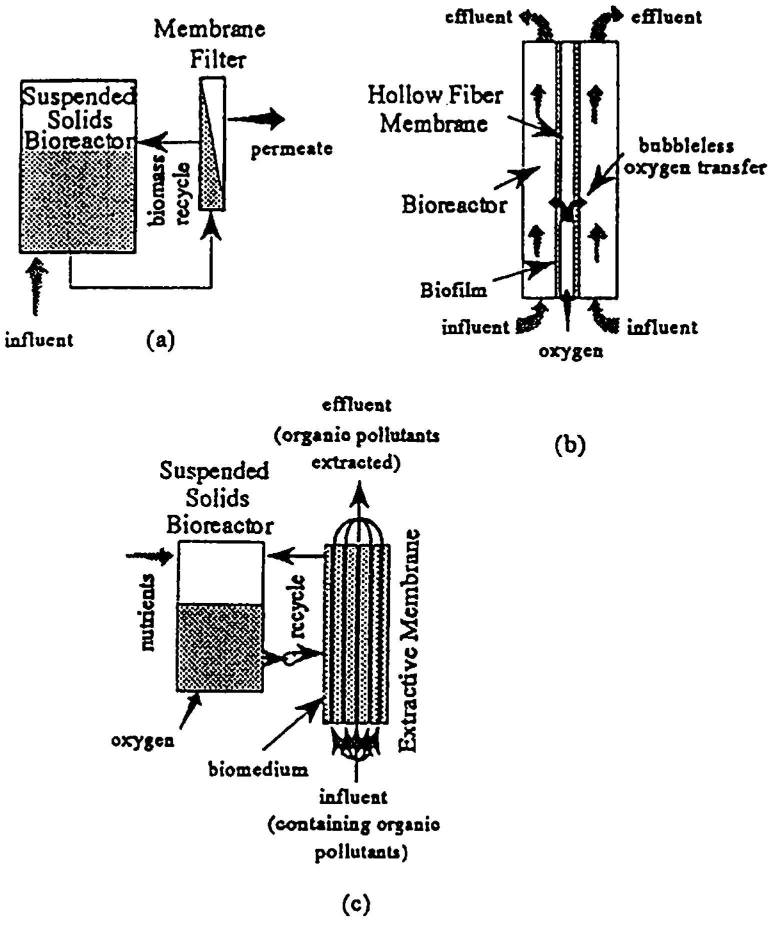


FIGURE 26 The main features of three different membrane bioreactor (MBR) processes: a) solid-liquid membrane separation bioreactor, b) bubbleless oxygen mass transfer, and c) extractive membrane bioreactor (Brindle [124])

and formaldehyde. The membrane bioreactor may also be applied for biogas production for energy purposes (see also section 2.3, Energy from Biogas). Gases produced by biodegradation in the liquid phase (CH_4 and CO_2) may be stripped through the membrane by pulling a vacuum on the reverse side (This principle is explained by degassing through a membrane contactor; see under c) and also sections 2.1.3 and 5.3.) Of the three types mentioned, only the solid liquid membrane bioreactor process is currently in commercial use with plants installed worldwide; see TableVIII. Such MBR's employ ultra- or microfiltration modules for the retention of and subsequent recycling of biomass to the bioreactor. The membrane processes, whether they are in combination with aerobic or anaerobic reactors, can be operated with the membrane unit placed in the reactor vessel or outside as a separate unit. With the membrane unit placed in the bioreactor unit, the return of solids to the reactor is avoided. This is also the principle of the Kubota membrane reactor illustrated in Figure 27[126]. As can be seen, the membrane unit is here placed in the bioreactor unit. The Kubota process was developed by Kubota Corporation Environmental Plant Division in Japan to meet the increasing market for compact module with low maintenance. The requirements was for a system capable of treating a wide range of effluents to a consistently high standard. The first pilot plant became operational in 1989 with the first operational plant being installed in 1991. The process has now been installed at a number of industrial effluent sewage and sludge treatment facilities in Japan. A pilot plant is also reported to be successfully operating at Wessex Water in Bath, UK (since April 1995) [126].

Fuch et al [127] is also reporting successful results using a biofilm reactor for intensive post-treatment of drinking water to remove micro-organisms and remnant carbon source. A nitrate permeable membrane was used and the denitrification would take place in the biofilm. The effluent met nearly all relevant criteria for drinking water. By pressurizing the aerobic sludge bioreactor the quality of drinking water with hardly any bacteria in the purified stream was obtained [128].

TABLE VIII

Examples of commercial-scale solid-liquid MBR process [124]

Company	Country	Type of Waste	No. of Plants	Capacity m^3d^{-1}
Rhône Poulenc-Techsep	France	Domestic	> 40	< 400
Thetford Systems	USA	Domestic	> 30	< 200
Kubota	Japan	Domestic	8	10-110
Degremont	France	Industrial	1	500
Membrantek	S. Africa	Industrial	2	100-500
Zenon Env. Inc	Canada	Industrial	1	116
Grontmij	Germany	Landfill	> 20	50-240
SITA/Lyonnaise des Eaux	France	Landfill	3	10-50

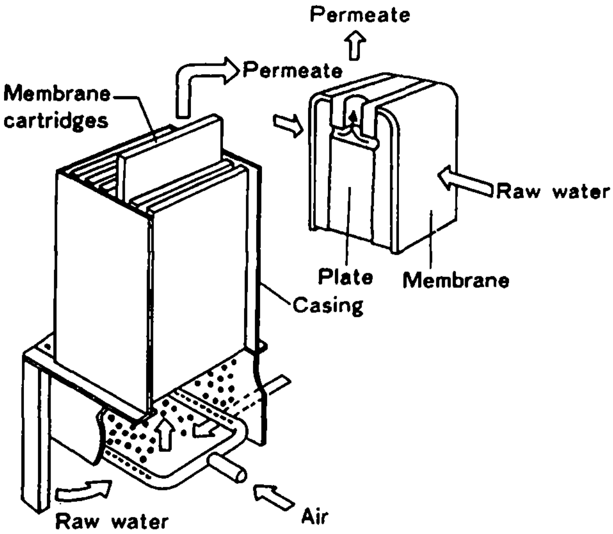


FIGURE 27 A schematic diagram of the Kubota membrane unit (bioreactor) operation and panel construction

(Churchouse [126]*, reprinted from Membr. Techn., 83, p.5, Copyright© (1997) with kind permission from Elsevier Science)*

c) *Removal of VOC through a Membrane Contactor*

Basic principle:

The principle for removal of volatile compounds from a liquid phase trough a membrane may be compared to a standard desorption process which takes place in a column. The separation performance in the membrane process is determined by the distribution coefficient of a component in two phases and the membrane acts only as an interface, similar to membrane distillation. The membrane process is more attractive than ordinary columns due to the large contact area available for permeation per volume which makes the modules very compact. Other advantages are the elimination of flooding and entrainment of the dispersed phase. A disadvantage is the adding of the membrane which may contribute to increased mass transfer resistance. The differential pressure across the membrane must be carefully watched so as not to exceed the wetting pressure. (See Figure 6 under section 2.1.3 for CO_2 removal). In any case, pressure control is very important in these desorption processes, and the desorption rate for removal may be enhanced either by pulling a vacuum on the gas side or using a stripping gas. If VOC is being removed, the VOCs must be condensed out from the stripping gas by cooling.

The membranes used for these contactors are usually (micro)porous, and made from hydrophobic materials like PTFE, PE or PP. The PDMS composite membranes are typically used for removal of VOC from air streams (see section 5.3). For other applications and novel developments, see also the section 2.2 "Bulk handling of oil".

Applications and Novel Developments:

A patented absorbent filled membrane is reported to improve the removal of VOCs from wastewater when used in a membrane contactor. The membrane in question is a pervaporation membrane comprising of a hydrophobic adsorbent (filler - activated carbon) uniformly dispersed in the polymer matrix. It thus combines the advantages of high sorption capacity of microporous hydrophobic adsorbents with the continuous operation of a membrane separation process [129].

Semi-volatile organic contaminants such as pesticides, PAHs and PCBs, may be removed by membrane-based solvent extraction using a non-volatile oil as the solvent. Experiments have been performed with a microporous hydrophobic polypropylene (PP) membrane (hollow fibers) and a water stream contaminated with the pesticide lindane and hexachlorocyclohexane. Results reported by Zander et al[130] showed that the two toxic components mentioned could be removed from the waterstream at the rate similar to that of the more volatile species. The solutes volatilize from water into the gas-filled membrane pores and are transferred to, and concentrated in, the oil phase. If successful on a larger scale, this process provides the opportunity for rapid removal of a wide range of organic compounds from water.

d) Removal of Heavy Metals from Industrial Waste Streams

Wastewaters and process waters from the electroplating and metal-finishing industries will often contain heavy metals. These metals must be recovered or removed for environmental and/or sometimes economic reasons. The membrane process usually applied is then a reverse osmosis (RO) process, and recoveries up to 95% have been obtained with high separations of most metal species. Spiral-wound modules are typically applied.[111]

Metalliferrous waste waters are generated from the production of a wide range of metallic articles, electronic components, zinc phosphating, mercury recycling and thermal galvanizing. A process which combines a pre-precipitation stage for formation of metal hydroxide flakes with a cross-flow membrane microfiltration can reach discharge levels approaching 0.05 mg per liter of dissolved solids. The metals to be removed are generally dissolved in the waste water, and by adding caustic solution they are converted into metal hydroxide flakes and pumped under pressure through a cross-flow membrane module (usually tubular membranes).

The latest development is however to try to remove these heavy metals by the use of bipolar membranes (electrodialysis). There is still a way to go before this is economically and technically feasible. Types of metallic ions and concentration of solution will have great influence. The problem is briefly discussed under the section 3.3 "Pulp and Paper" and 3.5.3 "Mining Industry". Comprehensive studies (lab.scale and pilot scale) using electrodialysis in the effluent for zinc hydrometallurgy industry are reported by Boucher et al[131].

5. GAS SEPARATION - PURIFICATION

The application of membranes for gas separation and purification is being discussed in various sections of this article:

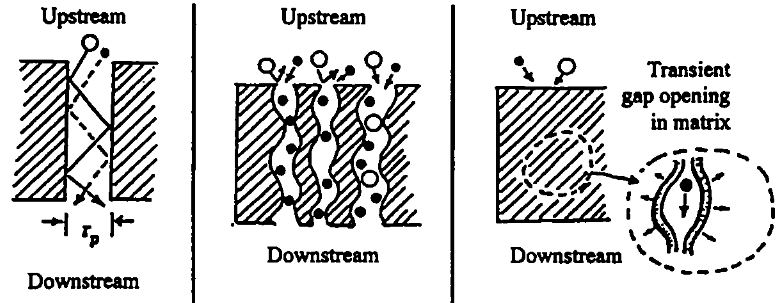
2 Energy Production (all sections),
3.1 Chemical and Petrochemical Industries,
3.2 Electrochemical Industries and
4.3 Removal of VOC.

In this current section a brief introduction will be given to the background and general applications of membranes for gas separation. Then, the main part will focus on "Novel Developments and Potential".

5.1 Background

In order to achieve successful membrane-based gas separation, demands are placed upon three supporting areas: 1) material selection 2) membrane formation and 3) modules and system configurations. More than in any other type of membrane separation process is the membrane itself an active element in the separation, and if the chemistry, possible interactions and material technology of the two elements gas - membrane is not fully understood, the separation may not be successful. A comprehensive introduction to the theory of gas transport and permeation in and through polymeric membranes are given in several textbooks [7,132,133,134] and review papers by Koros et al[135,136,137].

The main mechanisms of membrane-based gas separation are illustrated in Figure 28. Of these three mechanisms shown, solution-diffusion based transport through a



a) Knudsen flow separation is based on the inverse square root ration of the molecular weights of A & B

b) Ultramicroporous molecular sieving-separation is based primarily on the much higher diffusion rates of the smallest molecule, but sorption level differences may be important factors for similarly sized penetrants like O_2 & N_2

a) Solution-Diffusion-Separation is based on both solubility and mobility factors in essentially all cases. Diffusivity selectivity favor the smallest molecule. Solubility favors the most condensable molecule.

FIGURE 28 A schematic representation of the main mechanisms of membrane-based separations; a) Knudsen flow separation, b) Ultramicroporous molecular sieving separation and c) Solution-diffusion-separation
(Koros and Fleming[137]*, reprinted from J. Membr. Sci.,* *83, p.1, Copyright© (1993) with kind permission from Elsevier Science)*

polymer selective layer is used almost exclusively in current commercial devices. However the membrane contactors shown in Figure 6 and described in section 4.3 c, are mainly based on the Knudsen flow separation (Figure 28 a). By by of contrast, the latest development, the molecular sieve membranes, are separating according to the ultramicroporous sieving separation shown in Figure 28 b - these carbon membranes are expected to have a large potential for various challenging gas separations - a few modules are now commercial (see section "Novel Developments and Potential").

The polymeric membranes used for solution-diffusion based gas separation are either glassy*or rubbery* (i.e. operating process conditions are below or above the polymer's glass temperature Tg). The main percentage of membranes in use today are glassy polymers. These are often high performance materials with (relatively) high selectivies favoring a given component for permeation from the feed stream. Efficient solution-diffusion polymeric membranes rely upon the thermally agitated motion of chain segments comprising the polymer matrix, and the components will thus diffuse through the material by random jumps in transient gaps. Variations in the chemical nature of the polymer allows control of the relative extent of solution for the gases, and rate of diffusion of the various gases. (Permeability (P) is defined as diffusivity (D) x solubility (S); P = D x S)

5.2 Current Applications

The current applications within gas separation and purification are described in several sections of this article (2, 3.1, 3.2, and 4.3) These applications are mainly for air separation, hydrogen recovery, CO_2 removal from natural gas, dehydration, oxygen enrichment etc., and they are mainly based on glassy membranes. For gas purification related to removal of sour gases or volatile organic compounds, the rubbery membranes have been introduced and commercialized The main polymer to be mentioned for this purpose is the PDMS (poly-dimethyl-siloxane) which has a very high permeability to gases and vapors, and in general high selectivity for relevant gas pairs (see alsosection 2.2, Bulk Handling of Oil). The solution, diffusion and permeation of a variety of gases and vapors in PDMS have been reported by several authors [138,139,140].

5.3 Novel Developments and Potential

Some of the novel developments for gas separation with membranes are described in the sections: 2.1.3, 2.3.2, 3.1.3 and 3.2.2.

Main areas for novel developments within gas separation are the removal of acid and toxic gases, recovery of valuable inert gases, and hybrid process solutions (like integration of membrane modules in process streams like ammonia synthesis, magnesium production, biogas and olefin-paraffin separation in hydrocarbon processing). These separations are challenging and careful considerations must be given to possible degradation of the membrane material. Additionally it should be remembered that gases to be separated or purified in industrial process streams often are at elevated temperatures. This requires, in addition to chemical stability, thermally stable polymers. There are especially three groups of polymers which are suitable for separations at elevated temperatures: 1) new carbon membranes (elaborated on below), 2) perfluoromembranes[77] and 3) some polyimides[141]. In addition there are a few inorganic membranes, but inorganic membranes are usually too porous for gas separation. A few examples are however pointed at in this section; and also in section 3.1 there are a few mentioned in connection to dehydrogenation.

a) Polymeric Gas Separation Membranes

There is always a trade-off between permeability and selectivity for a gas pair in a polymeric membrane. The goal to aim for is high permeabilities and high selectivities for the separation in question, but up until now there seem to have been an upper bond in this relationship as illustrated in Figure 29[142]. Modifications of the existing materials and tailoring of new materials for specific separations will probably erase this "upper bond" (see Carbon Molecular Sieve Membranes, c).

For gas separations the prospect in future seem to be to use carriers (fixed site) for specific gases, membrane surface modifications, and molecular sieve membranes. The fixed site carrier membranes and the carbon membranes are especially in focus for the academic research, while the industry is apt to focus on solutions for improvement of existing membrane materials for instance by surface modifications. There is also the possibility of tailoring new membrane materials as illustrated with the examples in Figure 30[135]. Figure 30 a) shows a trade-off curve for the gas pair CO_2 /CH_4 in systematically varied group of polycarbonates. The abscissa is a log scale, so the deviations are significant. Figure 30 b) shows the trade-off curve for the

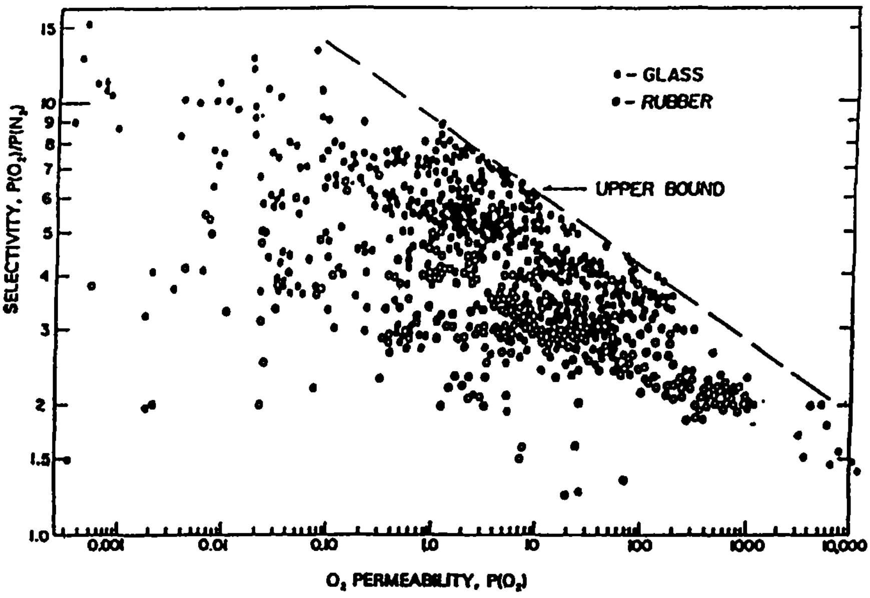


FIGURE 29 Hypothetical “upper bond” in the relationship between O_2/N_2 selectivity and permeability to O_2 for various rubbery and glassy polymers (Units for permeability coefficient: $P(O_2) \times 10^{10}$ $cm^3(STP)cm/s\ cm^2\ cm\ Hg$ (=Barrer). Temperature: 20-40°C)
(Robeson[142]*, reprinted from J. Membr. Sci., 62, p.165, Copyright© (1991) with kind permission from Elsevier Science)*

same gas pair, but now with points added connecting the related polycarbonate and polyimide structure. Both the permeability (for CO_2) and the selectivity (for the gas pair) have increased. It should be pointed out that these results only show the trend for the permeation through the different materials. The results shown in the figure are ideal; that is, they are reported for pure gases. For a gas mixture the permeabilities of the gases present will have a mutual influence on the transport through the membrane and the selectivity will (with a few exceptions) go down. The fixed-site-carrier membranes or facilitated transport membranes are discussed in section 2.1.3, CO_2-removal. Various types of amines have up until now been the

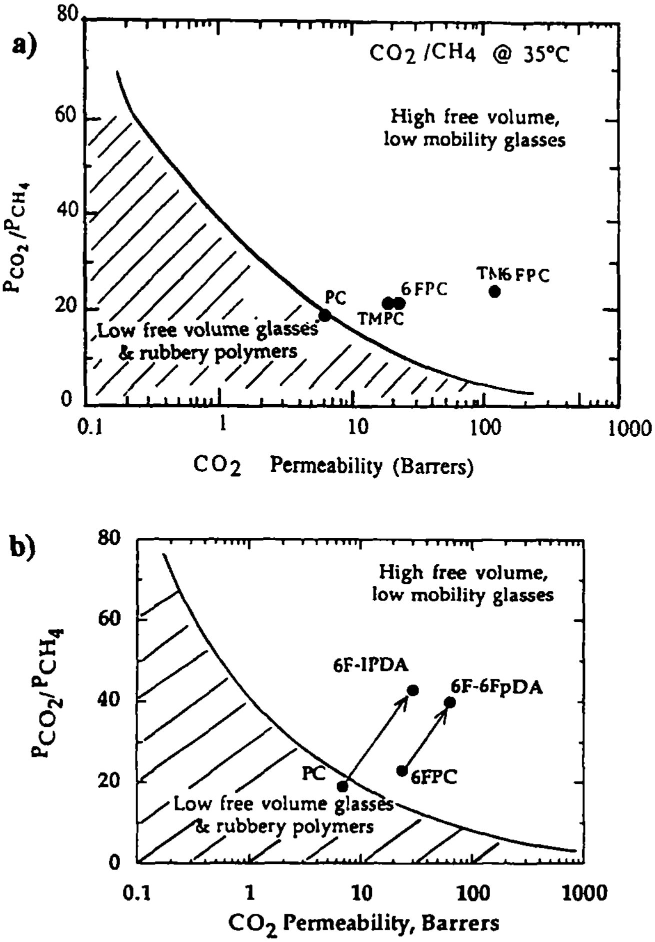


FIGURE 30 a) "Trade-off" curve for CO_2/CH_4 with the points added for systematically varied group of polycarbonates, illustrating the ability to deviate favourably from the standard trade-off curve behaviour. The abscissa is a log scale; hence the deviations are significant b) "Trade-off" curve for CO_2/CH_4 with the points added connecting related polycarbonate and polyimid structures

(Koros and Fleming ^{137}*, reprinted from J. Membr. Sci., 83, p.1, Copyright© (1993) with kind permission from Elsevier Science)*

most common absorbent for CO_2. This is the basic principle also for the purification of flue gases and natural gas with membrane contactors (same section. 2.1.3). The polymeric fixed site carrier membranes may also be prepared using amino groups for facilitated transport - these polymeric materials are however very difficult to synthesize and the development of these membranes are in an early stage.

A very special method which is recently patented should be mentioned [143]: The basic principle is the same as for a membrane contactor with a microporous hollow fiber membrane, with a liquid absorbent on one side (see section 2.1.3). The main difference is the liquid phase contains an oxidizing agent for the gaseous oxidizable constituents. In the patent it is documented that the absorption of the gaseous constituents and the subsequent oxidation/reduction reactions proceed so rapidly that a membrane gas absorption system based on redox reactions gives adequate mass transfer. Special gas components mentioned which are efficiently removed are: mercury vapor (from discharge streams or other process gas streams), unsaturated organic compounds, odor from discharge streams, H_2S from biogas/discharge gas. Various papers report treatment of sour gases with membranes [144,145,146] - including SO_2. SO_2 is present in flue gases to various degrees and in off gases from specific industries (like paper mills and power plants). There are various techniques for removal of sulfur compounds in gas streams, and up until now membrane technology has not been an attractive solution. However, with the focus on environmental problems in general and with the development of membrane modules for CO_2 removal, the possibilities for removal of SO_2 (and even NOx) in the same operation are being evaluated. The patent of UOP Inc.[144] from 1986 is describing the use of a multicomponent membrane comprising of polyethylene glycol and silicon rubber on polysulfone for separation of polar gases like H_2S, SO_2 and NH_3 from non polar gases. Chakma[145] has later used more or less the same membrane system, and he reports successful experiments using two liquid membranes in series for removal of CO_2 - SO_2 from flue gas. The membrane set-up consisted of an immobilized polyethyleneglycol (PEG 400) membrane in series with another immobilized diethanolamine (DEA)/PEG 400 membrane. SO_2 was then preferentially separated in the PEG 400 membrane while the DEA/PEG 400 membrane separated CO_2. Highest separation factors obtained for CO_2 and SO_2 were 220 and 140 respectively.

Another investigation was done by Weichart and Muller[146] using plasma polymerized membranes. The membranes were prepared from hexamethylsiloxane and hexamethyldisilazane and silicone rubber on porous supports of polyetherimide for the separation of mixtures of SO_2, NO_2 and CO diluted in N_2. They observed that the separation factors were substantially higher with the plasma polymer films than with silicon rubber. Although promising results are published, documentation of the durability of the membranes over time is missing. For the purification of SO_2 with membranes, it is always the question of the possible presence of water vapor - and if so, the gas will usually be very damaging to the membrane - it will degrade. Flue gases are usually hot gases and if membrane solutions shall be efficient, the actual process conditions must be carefully considered. Highly resistant perfluoromembranes have been developed, these may be suitable for aggressive environments - a few results are published[77].

Integrated membrane solutions may be a solution - dehydration and then SO_2 removal. The presence of water vapor is always crucial to membrane separation for aggressive gases like SO_2, HCl and Cl_2. Certain modifications of inorganic membranes may be considered.

b) Removal of VOCs from Air Streams

There are two efficient membrane methods for removal of VOCs from an air stream:

1) Permeation of VOC through a rubbery membrane (usually siloxane)
2) Absorption of VOC in a suitable absorbent using a membrane contactor

Recently a third method has been introduced:

3) Biodegradation of VOC in a membrane biofilter

In addition to the above mentioned type of membranes used, Cha et al[147] is reporting the efficient use of a dried, regenerated cellulose hollow fiber membrane for selective removal of water vapor and VOCs from a N_2-stream. The VOC components were toluene and methanol. The membrane tested was very selective for the extraction of moisture from the N_2-stream and for the removal of methanol (more than for toluene). Efficient membrane modules suitable for removal of VOC from air streams through a rubbery membrane has been developed at the research institute GKSS in Germany. Their system is based on pulling a vacuum on the permeate side; see Figure 31 where the basic considerations for the process lay-out are illustrated[37]. (See also sections 2.2 and 4.3) For larger gas streams a hybrid system of membrane stage and pressure swing absorption is recommended (see Figure 9)[148]. The standard membrane material for these modules (which are commercially available) is polydimethylsiloxane (PDMS) which has a very favorable permeation of the VOC-components compared to air (O_2 - N_2) as illustrated in Table IX.

A membrane contactor for removal of VOC is based on the same principle as for removal of CO_2 (see section 2.1.3) . The difference lies in the absorbent liquid. For efficient absorption of VOC is suggested using silicone oil and mineral oil. Experiments performed by Poddar et al [150] showed that a fairly high mass transfer coefficient was obtained for toluene, then followed methylene chloride, acetone and methanol. They also found that the membrane itself contributed significantly to the total mass transfer resistance. Their module was a microporous hollow fiber module. The advantage of this system compared to the use of activated carbon is that the absorbent is easily regenerated. (The regeneration of carbon is often a major cost in industrial applications.)

The removal of refrigerant gases (Freon gases) from air has also been tried with rubbery membranes. This has only been successful to a moderate extent.

The principle for membrane biofilters is described in section 4.3. The main applications for the biofilters are for removal of VOCs from liquid streams, however they may also be used for the removal of VOCs from air. Using a microporous hollow fiber membrane, the biofilm is attached to the outside of the fibers (permeate side) and the polluted air is fed to the inside. The VOCs will then permeate through the membrane and into the biofilm and degrade[151].

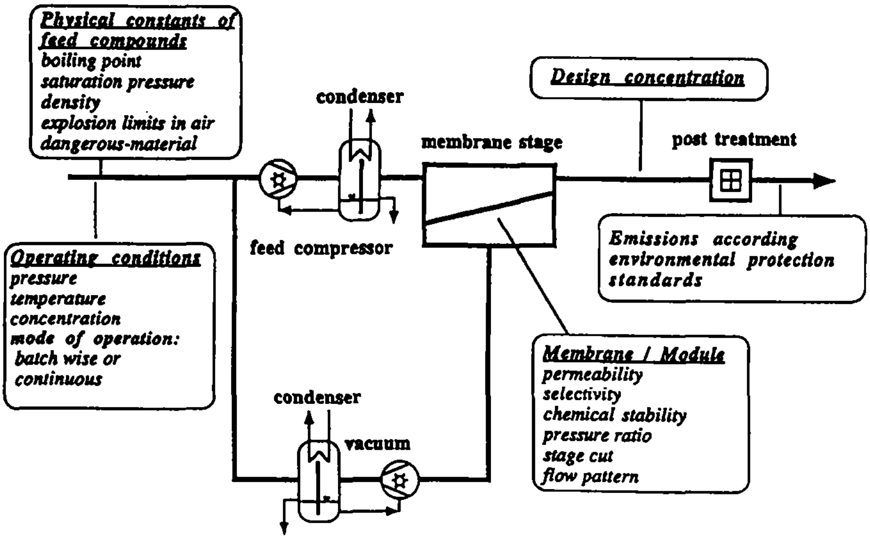


FIGURE 31 Illustration of basic considerations for the process lay-out for the removal of VOC from air streams with a rubbery membrane (Peinemann et al [37])

c) Carbon Molecular Sieve (CMS) Membranes

Carbon membranes for ultrafiltration and microfiltration of liquids have been available for commercial applications already for some years. The membrane construction is then usually a tubular membrane with a thin, porous layer of carbon applied to the narrow-diameter support tube built from a composite of carbon and carbon fiber. Great mechanical strength is then provided by the carbon fiber matrix, enabling the support tubes to withstand pressures greater than 50 bar even though wall thickness is only about 1.5mm (Scott, p. 141)[4].

The potential of using *carbon molecular sieving membranes in gas separation* is very promising, and these CMS-membranes offer many advantages for challenging gas separations; mainly by achieving high selectivities without losing productivity, and the possibility of using the membrane at very high process temperatures. The temperature resistance is strong for these carbon membranes and they are chemically

TABLE IX

Permeabilities of various components in polydimethylsiloxane at 40°C[149]

Component	Permeability (Barrer*)
nitrogen	280
oxygen	600
methane	940
carbon dioxide	3200
ethanol	53,000
methylene chloride	193,000
1,2 dichloroethane	269,000
carbon tetrachloride	290,000
chloroform	329,000
1,1,2-trichloroethane	530,000
trichloroethylene	740,000
toluene	1,106,000

*1 Barrer = 2.77×10^{-9} m^3(STP) m / m^2 bar h

resistant to acids at all concentrations, hot organic solvents and alkaline baths. They are vulnerable to oxidizing agents though.

The membranes are easily prepared by pyrolyzing polymeric precursor materials. A number of variables affect the pyrolysis process, and the pyrolysis conditions may dramatically influence the carbon membrane properties.

There are a few commercial carbon membrane modules available for gas separation, here is mentioned the producers Air Products, USA and Carbon Membranes Ltd. in Israel. The modules of Carbon Membranes are for instance prepared for the recovery of argon from oxygen, separation of CO_2 / CH_4, hydrogen recovery from lighter hydrocarbons and fluoride gases from mixtures with air (brochure).

The new CMS-membranes have expanded the potential for gas separation membrane applications dramatically. As illustrated in Figure 32 the upper-bond limit may no longer exist as suggested by Singh and Koros[152]. The very high selectivities indicated by the carbon membranes in this figure is referred to as "entropic selectivity" - which emphasizes that selectivity of these membranes are mainly controlled by the difference in diffusion rates based on size and shape of the gaseous components. The transport mechanisms in a CMS-membrane may be compared to that of a zeolite membrane. These two types of membranes have dissimilar chemical properties, but similar correlations between diffusivity and gas molecular diameters, thereby indicating that the barrier to diffusion is entirely due to repulsive forces involved in passing through the constricted regions of the micropores. A rough analogy to the molecular sieving process may be drawn from the theory of diffusion of gases in glassy polymer matrices[152].

Rao and Sirkar [153] have used a nanoporous carbon membrane for the separation of hydrogen - hydrocarbon gas mixtures, and studied the effect on hydrogen recovery and hydrocarbon rejection of pressure levels at high and low pressure sides of the membrane and the type of flow rate of sweep gas at the low pressure side. They found that membrane performance and hydrocarbon rejection increased significantly with increasing feed pressure. Not surprisingly, the H_2 recovery decreased with increasing feed pressure. With higher hydrogen sweep gas pressure, the recovery of H_2 increased and rejection of hydrocarbons decreased.

The selective removal of H_2S from an equimolar H_2S-H_2 stream is also reported. This current carbon membrane was nanoporous with selective surface flow (SSF)[154].

There is a main disadvantage reported for the CMS-membranes; the membranes are vulnerable to water vapor - the performance losses occur at all levels, increasing with increasing humidity levels[155,156].

The effect of gas temperature and pressure for CMS-membranes has been investigated by several. Damle et al[157] found a significant effect on separation properties for mixed gas separation. J.E. Koresh[158] has closely studied the effect of

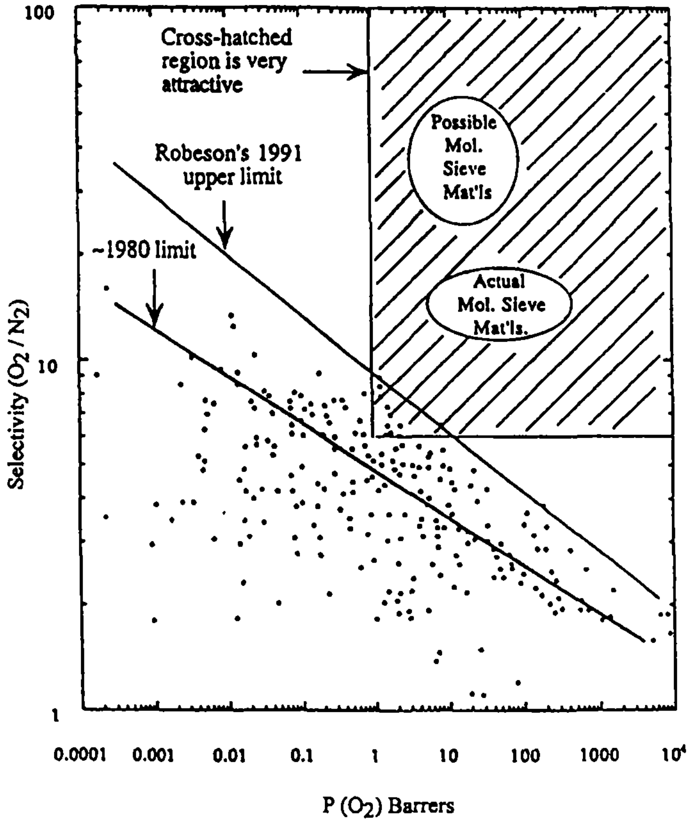


FIGURE 32 The trade-off curve of oxygen permeability and oxygen/nitrogen selectivity. The upper-bond curve still applies for ordinary polymeric materials, but molecular sieving materials like zeolites and carbon membranes lie above the upper bond (compare Figure 30) (Sing and Koros [152])

temperature on the flexibility of the carbon skeleton. He documents the great difference in the activation of the carbon matrix at different temperatures for various components ; hence the temperature effect on separation properties of the carbon membrane may be better understood.

One of the most interesting features of these CMS-membranes is their thermal resistance. CMS-membranes may be used at temperatures that have only been possible for inorganic membranes up until now. Results published by Jones and Koros [159,160] were obtained by using a polyimide precursor pyrolyzed under vacuum at temperatures as high as 500 and 550°C! The potential for these membranes is quite obvious in industrial applications where high temperatures and aggressive process conditions often are the situation.

Other results are published by Suda and Haraya[161] for selected gases with a pyrolyzed Kapton poyimide membrane. The permselectivities obtained were amazing, although this carbon membrane showed too low a permeability for practical industrial applications. The highest selectivity measured were H_2/N_2 4700, He/N_2 2800, CO_2/N_2 122, and O_2/N_2 36 respectively at 308 K. These results are to a certain extent confirmed by Petersen et al with the same membrane[162].

The carbon molecular sieve membranes will probably find many suitable gas separation applications in near future as the technique is developed and improved for larger modules suitable for application in process industries.

d) Inorganic Membranes for Gas Separations

Inorganic membranes are in general too porous for efficient gas separation although they are excellent for separations at elevated temperature. The ceramic membrane reactors do however have a very promising potential for specific separations (see section 3.1.3) The potential of using metallic membranes for gas separation is also briefly mentioned in the section of recovery of hydrogen (3.1.3).

An interesting module comprising of ceramic tubular membranes coated with polyphosphazene is reported by Peterson et al[163]. The membrane was tested over a temperature range of 80 - 270° C and for the separation of acid gases and organic chemicals from waste streams. The concept is interesting, but, not surprisingly, they observed degradation of the polymer at the higher temperatures. SO_2 was removed from a mixture with N_2 to a maximum of 23% at the highest temperature; and only to about 10% around 100°C.

Another membrane, Si-C-O, formed on the outer surface of an α-alumina support, coated with single-component polycarbonate and pyrolyzed, has been tested at permeation temperatures for H_2-N_2 at a temperature of 773 K. A selectivity of 18-63 was obtained, but the permeation rate was low at the higher temperatures suggesting that permeation was controlled by Knudsen diffusion[164].

A very interesting type of membrane is reported which has an absolute selectivity for oxygen. The non-porous membrane is based on mixed-conducting perovskites (a combination of LaO-Sr-MnO_3), and a permeability for O_2 of 10^{-10} mol/sec-cm^2 was measured at around 800^0C. This is considered to be an interesting membrane for industrial applications were high purity oxygen is demanded[165].

6. OTHER APPLICATIONS

Membranes are being widely used in a large variety of processes in addition to the chemical processes focused on in the previous chapters of this article; other main areas are food and beverages, pharmaceutical and biochemical industries and medicine. It is beyond the scope of this article to cover all these applications in detail. A brief summary pointing out the main areas for use of membranes in these industries will be given however, and the reader will be referred to more detailed books and review articles on the topics.

6.1 Food and Beverages

Membrane processes have for a long time played a significant part in the manufacturing industry for food and beverages, and in particular in the dairy industry. The advantages of using membrane technology in these industries include 1) low energy requirements and low costs 2) possibility of lower temperature processing (hence reduction of thermal damage to food during processing), and 3) simpler process design.

Ultrafiltration (UF) and reverse osmosis (RO) are still the dominant membrane separation techniques. Typical UF-applications are: 1) concentration/fractionation of whey proteins, 2) juice and wine clarification, 3) dewatering of egg-white and 4) separation of fermentation broth, while typical RO-applications are: 1) water treatment, 2) product and chemical recovery, 3) concentration of product streams and 4) clarification and recovery of flavors. Microfiltration (MF) is also being used for clarification and biological stabilization of beer and other beverages.

Reverse osmosis (RO) membranes have an excellent potential for expanded use in food processing as these membranes are improved. The crucial factors are 1) resistance to fouling, 2) membranes and modules that can withstand repeated steam sterilization, 3) membranes that can resist damage from chemicals such as chlorine and caustics, and 4) membranes and modules that can operate continuously at temperatures above 70^0C These demands are valid for all extended use of membranes in food industries.

Currently the biggest use of RO for food processing applications is within the dairy industry although recent advances has expanded the applications into several new areas (meat, poultry, and seafood applications, fruit and vegetable processing, beer and wine industries). Applications in dairy industry are aimed at enhancing the manifestation of desired functional properties of milk proteins, fractionating casein and whey proteins, enhancing the microbial quality of dairy fluids, upgrading the quality of low-quality whey, and standardizing milk. Not only RO-processes but combination of various membranes processes are used for these purposes.

A comprehensive review of current and future applications for membrane processes in the dairy industry has been presented by Rosenberg (1995)[166].

There is currently also much interest in the application of membranes in the agricultural fat and oil processing industry, both for oil refining and for the enzymatic modification of fats and oils using lipase due to the mild processing conditions compared with conventional technology. A good discussion of this topic was recently presented by Snape and Nakajima [167].

Another emerging application is the integration of membranes into sugar production. where the filtration steps then would be replaced by (integrated) membrane modules, mainly then UF or MF-membranes.

Reverse osmosis, ultrafiltration, nanofiltration and even electrodialysis are used extensively to ensure the safe production and quality maintenance of food products, and improvement in the microfiltration membranes have led to improvement of bacterial and hygienic qualities.

The problems related to filtration and fouling are much the same in food and dairy industries as in chemical process industries. Relevant references for this topic is pointed at in sections 3.3, 3.4 and 4 in this article.

For a general background and more comprehensive information on membranes in the industries for food and beverages, the reader is advised to study selected chapters in Ho & Sirkar[3], and Scott[4] and journals on membranes, food processing and filtration.

6.2 Pharmaceutical and Biochemical Industry

The pharmaceutical industry have found widespread use for membranes in sterilization, isolation, purification, concentration and particle removal processes. The need for higher product quality, greater measurability, validation and improved product output and scalability are among the driving forces affecting the increasingly use of membranes. The need for faster, more accurate and cost-efficient drug testing and development has required the use of membranes in microfiltration environments for human, animal and plant disease research and diagnostics[1].

In pharmaceutical industries the final product quality is often ensured by using membrane filter cartridges, and measurements at critical points where particles or microbes may contaminate a product, are therefore performed. Special membrane filters are available for various standard tests.

For medical applications membrane filtration is much used in laboratory. A good overview of analytical applications of membranes is given by Scott (section 8)[4] Suitable units are available in a wide array of different types for various applications such as: 1) sterile filtration of aqueous media and gases, 2) ultracleaning of small volume samples containing solvents, 3)preclarification of liquids containing coarse particles and 4) microbiological investigations, ibid.

Biochemical industries are in practice both laboratory scale processes used to clarify, concentrate and purify macromolecular products associated with a very low tolerance level of pollutants; but also processes on an industrial scale used for waste water treatment or production of biogas (see sections 2.3 and 4.3 in this article). Membranes in biochemical industry are also used as the separating device in analytical sensors to determine concentrations of certain components in a (fermentation) process .

Synthetic membranes are used for drug delivery in medicine; these applications are increasingly growing in importance.

Membranes in pharmaceutical and biotechnology applications are considered to be one of the fastest growing markets for membranes.

An excellent review of membranes in biotechnology is given by several.

These referred articles [168-174] cover major aspects of the topic; like giving a summary of membranes processes[168], discussing suitable materials and process design[169] and affinity membranes in bioseparation[170], new developments in membrane bioreactors[171], enzyme membrane bioreactors[172], recovery of volatile bioproducts by pervaporation[173] and the application of hollow fiber modules in medicine and biotechnology[174].

6.3 Medicine

Membranes are currently in use for various applications in medicine. Some of these are mentioned in section 6.2 such as membranes for drug delivery and analytical sensors. Two of the most common medical applications are the dialysis membranes for blood purification and the production of oxygen enriched air by the use of standard hollow fiber modules. Since many years different liver support systems have been evaluated clinically and in laboratory - interesting reports on these and other advancements for membrane technology in medicine is given by Gerner[174]. For more detailed information on membranes in medical applications the reader is referred to medical journals on the topic.

7. CONCLUSION

Membrane technology within chemical process industries is currently "proven technology" only within a few main areas; i.e. water purification and treatment of effluent streams, certain pervaporation processes for dehydration, high purity nitrogen production, dehydrogenation and specific processes with membrane electrolysis. However, membrane technology is presently being introduced into a wide variety of other applications, and there is clearly a very positive trend for the development of industrial membrane applications.

For applications related to water and wastewater treatment, the focus is partly on how to reduce fouling and improve water flux. Improvement of the membrane materials may be done by using various types of surface treatment. However, the trend shows that new applications in more harsh industrial environments often demands other types than standard hydrophilic materials for treatment of effluent streams. Another important development is the use of bipolar membranes for recovery of chemicals, likewise the combination of bioreactors and membranes both for waste treatment, but also for recovery of valuable energy.

For applications related to gas separation and purification, membrane technology has up until now been common only within a few areas. More than within liquid separation, the membrane material plays an active part in the transport of the gases through the membrane. Evaluating this trend, conventional polymeric materials appear to have only marginal room for improvements, although reactive surface flow modifications may be useful in some cases. With the development of new materials for facilitated transport however, carbon molecular sieve membranes, catalytic membrane reactors and mixed matrix materials, the potential for application of gas separation membranes is very promising.

For the development of membranes for industrial applications, both for gas and *liquid separations*, the focus is clearly on the often harsh process conditions the membranes are exposed to; i.e. high temperatures and pressures, aggressive environments etc. Thus the lifetime of the membrane must be well documented before commercialization - this is a major reason for the often slow progress of the development. Likewise, the cost of the candidate membrane materials must be acceptable in order to be commercially attractive.

Process solutions using integrated hybrid membrane systems will often be the best solution to a specific industrial separation problem; hence good engineering combined with in-depth knowledge of the membranes is important, indeed critical, for acceptance of the technology within chemical industrial processes.

In addition to the processes discussed in this article, other main areas for application of membranes are within the manufacturing industries for food and beverages, pharmaceutical and biochemical industries. It is beyond the scope of the present review also to cover this.

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8. DEFINITIONS

- **antropogenic;** that which is caused by human activities (ex. anthropogenic pollution)

- **composite membranes*** membranes with an asymmetric structure and composed of two (or at times three) different materials. The sublayer is frequently an assymetric membrane on which a thin toplayer is applied by special techniques, e.g. dipcoating, interfacial polymericzation, plasma polymerization. The support structure may also be a vowen material.
- **facilitated transport*** enhanced tranport of a certain solute due to the presence of a carrier which interacts specifically with the solute, i.e. carrier- complex diffusion dominates over free diffusion
- **fixed site carrier membrane** membrane with fixed carriers in the polymeric matrix, enhancing the transport as descirbed by facilitated tranport
- **glass transition temperature*** characteristic temperature of each polymer which indicates the transition from rubbery to glassy state
- **glassy materials*** materials in which the glass transition temperature is higher than the actual performance (operating) temperature. These materials are hard and tough and may possess good chemical and thermal stability. Well known materials are cellulosic esters such as cellulose acetate (CA), polyacrylonitrile (PAN), polysulfone (PS), polyethersulfone (PES), polyimide(PI)
- **grafted membrane** membrane made from a grafted copolymer; i.e. different kinds of groups are introduced into sidechains of the polymer, resulting in a material with very different properties than the original polymer. This second monomer may be attached to the main chain by chemical means (peroxides) or by radiation
- **hollow fiber module*** module consisting of hollow fibers with a diameter smaller than 0.5 mm. The construction is the same as a capillary module
- **hydrophilic membrane*** membrane from a highly polar material with a high affinity for water. Examples are cellulosic esters, polyvinyl alcohol, aliphatic polyamids (nylons).
- **hydrophobic membrane*** membrane from a highly apolar material with a very low affinity for water. Also the wettability for water is very bad. Examples are

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* Definitions according to the "European Membrane Guide" by Mulder et al (1997)[175]

teflon (polytetrafluorethylene), polyethylene, polypropylene and polyvinylidenfluoride.

- **pervaporation*** process used to separate organic liquid mixtures such as azeotropic mixtures. A liquid feed mixture is put in contact with a membrane while at the permeate side a reduced pressure is applied by condenser, carrier gas or vacuum pump. The driving force is a partial pressure difference. generally composite membranes are applied with a dense (nonporrous) toplayer.
- **rubbery materials** materials in which the glass transition temperature is *lower* than the actual performance (operating) temperature. These materials are rubbery and may possess good chemical and thermal stability.

  Well known materials are polydimethylsiloxane (PDMS), polybutadiene (PB), polyethylene (PE)
- **spiral wound module*** module configuration in which two membranes and permeate spacer are sealed along three edges to have an envelope. This envelope is then together with feed spacer rolled around a central pipe.
- **stage cut** term used in gas separation instead of recovery; recovery (S) being defined as the fraction of the feed stream allowed to permeate through the membrane; i.e. the permeate feed ratio
- **Wobbe-index** quantitative index to compare quality of fuels [Btu/ft^3 or MJ/m^3]. Two fuels with the same Wobbe index will deliver the same amount of heat.

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