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Status review on membrane systems for hydrogen separation

Intermediate report EU project MIGREYD NNE5-2001-670

S.C.A. Kluiters

Acknowledgement/Preface

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Abstract

This report summarizes the state of the art of membrane techniques for separation of hydrogen from other gases, for application within IGCC-processes fuelled with refinery residuals and biomass.

Although the number of hydrogen selective membrane applications is currently still rather limited, research is performed to increase the range of applications.

The properties of the flow to be separated are the starting point to select a suitable membrane. For a preliminary choice of a membrane type, the operating temperature ranges can be used, although the feed composition and cost should also be taken into account. Once the membrane is selected, a membrane module can be chosen or designed taking into account considerations such as manufacturability, maintainability, operability, efficiency, membrane deterioration, and costs. Modules can be combined to form stages. By combining multiple stages and adding features, a range of membrane systems can be designed. This versatility greatly adds to the attractiveness of membrane systems.

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SUMMARY

The EU supported MIGREYD project, an acronym for Modular IGCC Concepts for In-Refinery Energy and Hydrogen Supply, intends to strengthen the position of IGCC technology focussing on:

1) the conversion of low-value oil refinery residues to useful clean energy, and
2) hydrogen production.

ECN's major role in this project is work package 3, which analyses the environmental benefits of integrating an IGCC into an oil refinery. The main objectives of WP3 are the reduction of CO_2 emissions and a study into the possibility of application of membrane systems for hydrogen separation. The first objective, a reduction of CO_2 emissions may be achieved by co-gasification of biomass and by application of SOFC systems within the IGCC process. The status review presented in this report is a first step towards possible application of hydrogen selective membranes for separation of hydrogen from other gases produced within the IGCC cycle, the second objective of WP3. Other separation technologies that could be used are pressure swing adsorption (PSA) and cryogenic separation. However, these last two options are not studied in this report. This study will serve as the basis for systems studies to be performed later on in this project.

In the last 50 years there have been strong developments in membrane technology for gas separation. Currently the number of hydrogen selective membrane applications is still limited to two, and both applications are not in critical parts of the process. These two are hydrogen recovery from off-gases in the ammonia industry and production of pure hydrogen in the electronics industry. Research is going on, intended to apply hydrogen selective membranes in more critical parts of processes.

Different types of hydrogen selective membranes are presented for hydrogen separation from refinery off-gases and separation of hydrogen from syngas. Each membrane has its own operating ranges, in terms of temperatures and flow compositions. The properties of the flow to be separated are therefore a starting point to select a suitable membrane. Table 1 presents the properties of the most important membranes that can be used for hydrogen separation processes.

Once the membrane type is selected, the membrane module can be chosen or designed taking into account considerations such as manufacturability, maintainability, operability, efficiency, membrane deterioration, and costs. Currently five module types exist, plate-and-frame and spiral-wound modules, based on flat membranes, and tubular, capillary and hollow-fibre modules, based on tubular membrane geometries.

Modules are combined into stages. The options for membrane system layout are virtually endless, as stages can be combined in various ways, and processes can be changed by adding compressors and recycles. The membrane system design also needs to accommodate occasional cleaning/replacement and possibly carrying out of chemical reactions.

Table 1: *Properties of the relevant hydrogen selective membranes*

	Dense polymer	Micro porous ceramic	Dense metallic	Porous carbon	Dense ceramic
Temperature range	<100 °C	200-600 °C	300-600 °C	500-900 °C	600-900 °C
H_2 selectivity	low	5-139	>1000	4-20	>1000
H_2 flux (10^{-3} mol/m^{2}s) at dP=1 bar	low	60-300	60-300	10-200	6-80
Stability issues	Swelling, compaction, mechanical strength	Stability in H_2O	Phase transition	Brittle, oxidising	Stability in CO_2
Poisoning issues	HCl, SO_x, (CO_2)		H_2S, HCl, CO	Strong adsorbing vapours, organics	H_2S
Materials	Polymers	Silica, alumina, zirconia, titania, zeolites	Palladium alloy	Carbon	Proton conducting ceramics (mainly $SrCeO_{3-\delta}$, $BaCeO_{3-\delta}$)
Transport mechanism	Solution/ diffusion	Molecular sieving	Solution/ diffusion	Surface diffusion; molecular sieving	Solution/ diffusion (proton conduction)
Development status	Commercial by Air Products, Linde, BOC, Air Liquide	Prototype tubular silica membranes available up to 90 cm. Other materials only small samples (cm^2)	Commercial by Johnson Matthey; prototype membrane tubes available up to 60 cm	Small membrane modules commercial, mostly small samples (cm^2) available for testing	Small samples available for testing

1. INTRODUCTION

The EU supported MIGREYD project, an acronym for Modular IGCC Concepts for In-Refinery Energy and Hydrogen Supply, intends to strengthen the position of IGCC technology focussing on:

1) the conversion of low-value oil refinery residues to useful clean energy, and
2) hydrogen production.

ECN's major role in this project is work package 3, which analyses the environmental benefits of integrating an IGCC into an oil refinery. The main objectives of WP3 are the reduction of CO_2 emissions and a study into the desirability of application of membrane systems for hydrogen separation. The first objective, a reduction of CO_2 emissions may be achieved by co-gasification of biomass and by application of SOFC systems within the IGCC process. The status review presented in this report is a first step towards possible application of hydrogen selective membranes for separation of hydrogen from other gases produced within the IGCC cycle, the second objective of WP3. Other separation technologies that could be used are pressure swing adsorption (PSA) and cryogenic separation. However, these last two options are not studied in this report. This study will serve as the basis for systems studies to be performed later on in this project.

This report summarizes the state of the art in hydrogen gas separation membrane technology. Chapter 2 gives a general introduction to membranes, where nomenclature, definitions, transport mechanisms and manufacturing technology are presented. The most important membranes for hydrogen separation from refinery off-gases and separation of hydrogen from syngas, a mixture of hydrogen and carbon monoxide, are presented in chapter 3. Chapter 4 provides an introduction to the design of membrane systems. In chapter 5 some conclusions are drawn.

2. GAS SEPARATION MEMBRANES

2.1 Introduction

A membrane is a barrier that permits selective mass transport between two phases. It is selective because some components can pass the membrane more easily than others. This makes membranes a suitable means to separate a mix of components. The phases on either side of the membrane can be liquid or gaseous. Although we may not be aware of their presence, membranes play an important role in life. Probably the best-known example of a membrane is the human skin. The skin admits selective transport of both gases and liquids (e.g., water can't flow in but it can flow out when sweating).

Membrane development started with liquid phase separation processes. Nollet performed the first known recorded membrane experiment in 1748, using a piece of pig's bladder as membrane. On one side of the membrane he had a vessel containing 'spirits of wine' and on the other side water. As the water permeated through the bladder faster than the wine the volume of the vessel increased whereas the amount of water (diluted with wine) on the other side of the membrane decreased (Mason, 1991). Development of gas separation membranes started later. The first large-scale gas separation membrane process was used in the mid-1940s by the United States government to separate UF_6 isotopes for nuclear fuel enrichment (Noble, 1995). The first commercially significant gas separation membranes were introduced only in late 1979. However, within 10 years a range of gas separation membranes has been developed (Noble, 1995).

In the last 50 years there have been strong developments in membrane technology, making application of manufactured membranes a viable option. Today's membrane applications are very diverse, ranging from reverse osmosis (to produce clean water) to micro filtration (to filter bacteria). Membranes owe their popularity largely to the following advantages (Mulder, 2000):

- (generally) low energy consumption;
- possibility to carry out separation continuously;
- mild process conditions;
- easy scaling up;
- absence of additives;
- possibility to combine with other separation technologies.

Important disadvantages are, depending on the specific membrane type:

- fouling tendency;
- low membrane lifetime;
- low selectivity or flux;
- more or less linear up-scaling factor (whereas competing processes exhibit economies of scale).

In this report only gas separation membranes are studied, i.e. membranes with gaseous phases on both sides. This is because membrane applications in the Migreyd project are limited to hydrogen selective membranes. Even though conditions in refineries and IGCCs may be somewhat extreme (in terms of pressures and temperatures), hydrogen will not be present in liquid form and it will not be (in large quantities) dissolved in liquids from which it should be separated.

2.2 Membrane nomenclature and classifications

Figure 1 illustrates the nomenclature used for membranes. The two sides of the membrane are called feed side (or upstream side) and permeate side (or downstream side). In practice, permeation can take place in both directions. Generally speaking, feed side and permeate side are chosen consistent with the rule that the permeation of the (most) relevant species takes place from feed to permeate side. The feed side flow is initially called the feed flow. The flow resulting after permeation is called retentate (or residue) flow. On the permeate side the inlet flow is called sweep flow and the exit flow permeate flow.

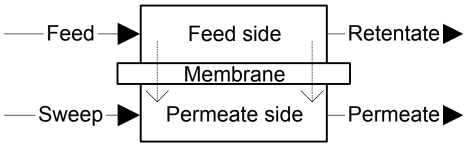

Figure 1: *Membrane unit nomenclature*

Performance and efficiency of membranes are usually measured in terms of flow (or flux) through the membrane and membrane selectivity towards mixtures. The flow can be measured in volume or mass per time unit (if measured per unit of surface it is called flux). The selectivity is a measure for the difference in permeabilities (the relative ease with which species can permeate) of different components. In other words, it is a measure for the membrane separation effectiveness. The selectivity factor $\alpha_{A/B}$ of two components A and B in a mixture is defined as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} \tag{2.1}$$

where y_A and y_B are the fractions of components A and B in the permeate and x_A and x_B are the fractions of the components A and B in the feed. A and B are usually chosen in such a way that the selectivity factor is greater than unity. If the selectivity factor is equal to one, there is no separation. The higher the selectivity factor, the more selective the membrane is to certain species (which is usually a desirable membrane property).

Two other important ratios to describe membrane performance are the recovery and volume reduction. The recovery or yield (S) is the fraction of the feed flow passing through the membrane:

$$S = \frac{q_p}{q_f} \tag{2.2}$$

where q_p is the permeated flow and q_f is the feed flow. The volume reduction (VR) is the ratio of the initial feed flow rate and the retentate flow rate:

$$VR = \frac{q_f}{q_r} \tag{2.3}$$

To subdivide membranes, a number of membrane properties can be used. One is the material the membrane is made of. So-called organic membranes are made of polymers. The group of inorganic membranes comprises membranes made of glass, metal (including carbon), and ceramics (including zeolites).

Another property of membranes used for subdivision, is the membrane structure and connected to this the way in which transport through the membrane takes place. Porous membranes enable transport through their pores, whereas dense membranes allow transport through the bulk of the material.

Finally, the morphology or structural make-up of membranes can also be used for classification. Symmetrical membranes have a homogeneous structure. Asymmetric membranes consist of several layers with different characteristics. There can also be a gradual transition from a dense membrane to a porous support. Membranes consisting of different layers of different materials are called composite membranes.

2.3 Gas separation mechanisms

As noted before, there are two main membrane permeation mechanisms: through the bulk of the material (dense membranes) and through pores (porous membranes). In the following sections, a number of membrane transport mechanisms are described. The mechanisms described are not limitative. Dense membranes usually have high selectivities, yet low fluxes. This principle also applies to small-pore membranes. Larger pores will increase the fluxes, but decrease selectivities.

2.3.1 Dense membrane separation mechanism

The *solution/diffusion mechanism* is the most commonly used physical model to describe gas transport through dense membranes. A gas molecule is adsorbed on one side of the membrane, dissolves in the membrane material, diffuses through the membrane and desorbs on the other side of the membrane. If diffusion through the membrane takes place in the form of ions and electrons (= proton exchange transport) or as atoms (e.g. for hydrogen transport through dense metal), the molecule needs to split up after adsorption and recombine after diffusing through the membrane.

2.3.2 Porous membrane separation mechanisms

Four types of diffusion mechanisms can be utilized to effect separation in porous membranes (see Figure 2) (Noble, 1995). In some cases, molecules can move through the membrane by more than one mechanism. These mechanisms are described below. Knudsen diffusion gives relatively low separation selectivities compared to surface diffusion and capillary condensation. Shape selective separation or molecular sieving can yield high selectivities. The separation factor for these mechanisms depends strongly on pore size distribution, temperature, pressure and interactions between gases being separated and the membrane surfaces.

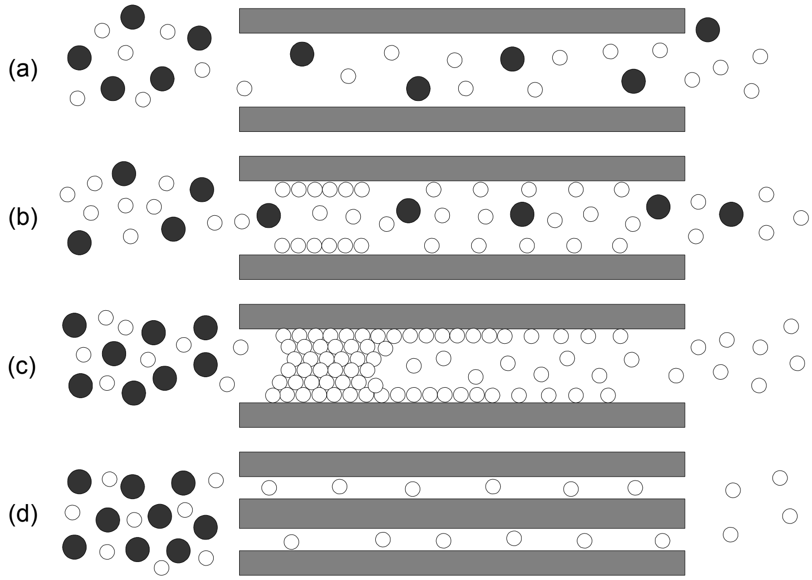

Figure 2: *Transport mechanisms in porous membranes: (a) Knudsen diffusion, (b) surface diffusion, (c) capillary condensation, (d) molecular sieving*

Knudsen (or free-molecule) diffusion (see Figure 2a) is said to appear for large Knudsen numbers. The Knudsen number Kn is defined as the ratio of the mean free path of the gas molecules (average distance between collisions) and a representative physical length scale (e.g., the pore radius).

$$Kn = \frac{l}{L} \tag{2.4}$$

If the pore radius is used as representative physical length scale the mean free path lengths are substantially higher than pore radiuses at Knudsen numbers larger than 10. The result is that mainly the lighter molecules permeate through the pores. Selectivity, however, is limited and can be calculated with the square root of the ratio of the molar masses of the gasses involved (Paul, 1994). The smaller the Knudsen number, the larger the pores become (relative to the mean free path of the gas molecules), the lower selectivity becomes. For Knudsen numbers < 1 the dominant transport mechanism is *viscous flow,* which is non-selective.

Surface diffusion (see Figure 2b) can occur in parallel with Knudsen diffusion. Gas molecules are adsorbed on the pore walls of the membrane and migrate along the surface. Surface diffusion increases the permeability of the components adsorbing more strongly to the membrane pores. At the same time, the effective pore diameter is reduced. Consequently, transport of non adsorbing components is reduced and selectivity is increased. This positive contribution of surface diffusion only works for certain temperature ranges and pore diameters.

Capillary condensation (see Figure 2c) occurs if a condensed phase (partially) fills the membrane pores. If the pores are completely filled with condensed phase, only the species soluble in the condensed phase can permeate through the membrane. Fluxes and selectivities are generally high for capillary condensation. The appearance of capillary condensation, however, strongly depends on gas composition, pore size, and uniformity of pore sizes.

If pore sizes become sufficiently small (3.0-5.2 Å), *molecular sieving* (see Figure 2d) can be used to separate molecules that differ in kinetic diameter: the pore size becomes so small, that only the smaller gas molecules can permeate through the membrane.

2.4 Manufacturing techniques

All kinds of materials such as ceramic, glass, metal or polymers can be used for preparing membranes. The aim is to modify the material by means of an appropriate technique to obtain a membrane structure with morphology suitable for a specific separation. The material limits the preparation techniques employed, the membrane morphology obtained and the separation principle applied. In this section the most important membrane manufacturing techniques for gas separation membranes are presented. A more extensive review of manufacturing techniques is presented in (Mulder, 2000).

Sintering involves compression of powders and subsequent formation of solids from the particles by sintering at elevated temperatures. As the particles are not cubically shaped, pores will result. It is a very simple technique to prepare porous organic as well as inorganic materials with pore sizes ranging from 0.1 to 10 μm, the lower limit being determined by the minimum particle size. It is primarily suitable for materials with very high chemical, thermal and mechanical stability. A drawback is, however, that only certain types of membranes can be prepared by means of sintering. Besides, the porosity (pore area as fraction of total area) of porous polymeric membranes is generally low, in the order of 10 to 20%.

Higher porosities (up to 90%) can be achieved using *stretching*. This technique involves extension of an extruded film or foil made from a partially crystalline polymeric material. The extension is performed perpendicular to the direction of the extrusion. The result is that crystalline regions are located parallel to the extrusion direction. Small ruptures occur if mechanical stresses are applied, resulting in a porous structure. Pore sizes are in the range between 0.1 and 3 μm. This technique can only be used to manufacture membranes from (semi) crystalline polymeric materials.

Track-etching comprises tracking (the subjection of a film or foil to perpendicular high energy particle radiation) and subsequently etching away polymeric material along the tracks obtained by immersing the film in an acid or alkaline bath. The results are practically cylindrical pores with a narrow pore size distribution. Pore size can be obtained in the range from 0.02 to 10 μm. Surface porosity, however, is low (maximum 10%). This method is mainly used for organic materials, although it can be used for a limited number of inorganic materials too.

Template leaching can be used to create porous glass membranes. It involves the creation of a structure with a soluble and a non-soluble phase. The soluble phase is subsequently leached out using an acid or base. A wide range of pore diameters can be obtained, with a minimum of 5 nm (1 nm = 10^{-9} m). Templates are also used to prepare zeolite membranes. A support is immersed in a water-based sol containing silica, sodium hydroxide and the organic template. During heating, the zeolite crystals grow. Finally, the template is burned out (Vos, 1998).

Phase inversion is the most frequently used method for the current range of commercially available polymer membranes. In this method a polymer in a liquid state is transformed into a solid state, creating a membrane. Usually, the liquid state is first transformed into two separated liquids. During this so-called demixing stage, one of the liquids solidifies into a solid matrix. This method can be used to prepare both porous and non-porous membranes. The concept of phase inversion includes techniques such as solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation from the vapour phase and immersion precipitation. The majority of the phase inversion membranes are prepared by immersion precipitation (Ribberink, 1993).

Coating methods are especially important for dense polymeric membranes and inorganic composite membranes. Because the fluxes are generally lower for dense membranes than for porous membranes, membrane thickness needs to be minimized (see also section 4.2). To attain structural strength for reduced membrane thicknesses, composite membranes are used (the membrane is supported by a porous sub layer). A number of coating procedures in use are dip coating, plasma polymerisation, interfacial polymerisation, and in-situ polymerisation.

The *sol-gel* process was the first process to enable pore sizes in the nanometer range for ceramic membranes. In this process, an alkoxide precursor is formed into a gel via either the colloidal suspension route, or the polymeric gel route. In the colloidal suspension route, the precursor is hydrolysed to form a sol (a colloidal dispersion of particles in a liquid). By changing the surface charge of the particles in the sol or by increasing the concentration the particles tend to agglomerate and a three-dimensional network structure, a so-called gel is obtained. In the polymeric gel route a precursor is hydrolysed slowly to form an inorganic polymer and finally a polymer network. The most difficult step is drying the gel, which can result in crack formation. The final step in the process is sintering.

Even smaller pore sizes can be obtained by densification of the mesoporous structure. Some surface modification techniques for ceramic membranes are internal deposition of pores by monolayer or multi-layer, pore plugging of nanoparticles, coating an inorganic polymeric gel layer on top of a support and constrictions at sites in the top layer by *Chemical vapour deposition* (CVD). With CVD a metal organic component is vaporised in the carrier gas, which enters from one side of the membrane and the other reactant enters from the other side of the membrane. Reactants diffuse into the pores and react there. The product is deposited on the pores. Depending on the structure of the material and the process parameters the deposited layer will be dense or (micro)porous.

Metals can be also be deposited on a substrate layer by means of *physical vapour deposition* (PVD). In this process, the solid material to be deposited is first evaporated in a vacuum system using physical techniques. The thin to medium thickness film is subsequently condensed and deposited on the cooler substrate (Shu et al., 1991).

Somewhat thicker metallic membranes can also be prepared by means of *alloy casting and rolling*. This is the standard practice for large scale manufacturing of metallic plates and sheets and together with electroless plating (see below) it is the method most commonly used for preparation of metallic membranes. The process involves melting raw materials at very high temperature, ingot casting, high-temperature homogenisation, hot and cold forging or pressing, followed by repeated sequences of alternate cold rolling and anneals, down to the required thickness. If the cooling speed of the melts is chosen fast enough, this method can also be used to obtain amorphous metals called metallic glasses. This method may be suitable for thin membranes if the metal purity is high enough, because contamination becomes a problem as metal foils become thinner (Shu et al., 1991).

Other techniques to deposit thin layers on substrates are *electroless plating* and *electroplating*. Electroless plating is based upon the controlled autocatalyzed decomposition or reduction of metastable metallic salt complexes on target surfaces. In the case of production of palladium membranes the substrate should be preseeded with palladium nuclei in an activation solution to reduce the induction period of the autocatalytic plating reaction. In electroplating, the substrate acts as cathode. In a plating bath, the metal or an alloy is coated on the substrate (Shu et al., 1991).

Pyrolysis involves degrading polymers that are coated on porous supports. This method can be used to prepare silica and carbon molecular sieves from silicone rubbers and thermosetting polymers respectively (Ribberink, 1993).

3. HYDROGEN SELECTIVE MEMBRANES

3.1 Introduction

For separation of hydrogen from gaseous streams, membranes can provide an attractive alternative to PSA and cryogenic separation, depending on the scale and purity of the product streams required. There are currently two applications in which hydrogen selective membranes are used. Since 1979 polymeric membranes are used in the ammonia industry for hydrogen recovery from off-gases and in the second half of the 1990s a new application appeared: the production of pure hydrogen in the electronics industry using palladium membranes. Pilot projects are currently under way to demonstrate the technical feasibility of hydrogen selective membranes in other applications, more at the heart of processes. Both refineries and IGCCs may be good candidates for hydrogen selective membrane applications, as they possess gaseous streams relatively rich in hydrogen.

Hydrogen selective membranes can be broadly separated into four categories: polymeric (organic), metallic, carbon and ceramic (the latter three jointly called inorganic). For a long time, considerably more effort has been put in development of polymeric membranes than in inorganic membranes. Consequently polymeric membranes have wide ranging applications and can be bought at relatively low cost. However, interest in inorganic membranes has started to grow in the last decade. Inorganic materials can operate under higher temperatures than polymeric materials and generally possess superior chemical stability relative to polymeric materials. Ceramics form the main class of inorganic membranes (Mulder, 2000).

The following sections provide an overview of the current status of the various hydrogen selective membranes. The information is mainly taken from (Delft et al., 2003). The main properties such as the transport mechanisms, the range of possible working conditions, development status, and strong and weak points of the various types of hydrogen permeating membranes are presented. To characterise the membranes the material of which they are made is used. A summary of the properties, and advantages and drawbacks of the most important hydrogen permeating membranes is presented in section 3.7.

3.2 Polymeric membranes

Polymeric membranes are a dense-type of membranes, transporting species through the bulk of the material. Depending on their state, polymeric membranes can be subdivided into glassy (prepared at temperatures below the glass transition temperature) and rubbery (prepared at temperatures above the glass transition temperature) polymeric membranes. Glassy membranes have relatively high selectivity and low flux, whereas rubbery membranes have increased flux but lower selectivity. In absolute terms both types have moderate fluxes and selectivity. They are usually produced using the phase inversion method.

Operating temperatures are limited to 90-100 °C. Advantages in most applications are good ability to cope with high pressure-drops, low cost, and good scalability. Possible problems are limited chemical resistance to certain chemicals such as HCl, SO_x, but also CO_2, limited mechanical strength, and relatively high sensitivity to swelling and compaction.

Polymeric membranes are in an advanced stage of development. Polymeric membranes for hydrogen separation are commercially available from gas producing companies like Air Products, Linde, BOC and Air Liquide.

3.3 Metallic membranes

If very pure hydrogen is required, dense metallic membranes may be a good option. Especially palladium and palladium alloys (practically the only types of hydrogen selective metallic membranes used) are extremely selective as only hydrogen can permeate through them.

Hydrogen transport through the membrane can best be described by the solution/diffusion mechanism: hydrogen is adsorbed on one side of the membrane, splits into two atoms, diffuses through the metal matrix, and recombines and desorbs at the permeate side. Fluxes are moderate. To improve fluxes (see section 4.2) and reduce membrane cost (material cost of palladium is very high), usually thin layers deposited on a porous ceramic or metallic support are used.

If palladium membranes are exposed to hydrogen at lower temperatures, they can be seriously damaged, because hydrogen can become locked inside the palladium lattice. This will cause stresses in the membrane, increasing the likelihood of membrane failure. A solution to this problem is to dope the palladium with other elements such as silver or copper. Operating temperatures of the today's palladium alloy membranes are in the range 300-600 °C.

A major technical disadvantage of palladium membranes in most applications is their high sensitivity to chemicals such as sulphur, chlorine and even CO. These chemicals can poison the membrane surface reducing the effective hydrogen fluxes by 20 to even 100%. Although much attention is focused on development of palladium membranes, their commercial availability is still limited. Johnson Matthey produces palladium-silver alloy membranes up to 60 cm in size commercially for the production of ultra pure hydrogen in the electronics industry (Delft et al., 2003).

3.4 Carbon membranes

There are two types of carbon membranes, applying different transport mechanisms: molecular sieving and surface diffusion membranes.

Molecular sieving membranes are identified as promising, both in terms of separation properties (including achievable fluxes) and stabilities, but are not yet commercially available at a sufficiently large scale. The pore sizes are in the order of the size of H_2-molecules. Reported selectivities are in the range of 4-20.

Adsorption selective carbon membranes separate non- (or weakly) adsorbable from adsorbable gases (such as H_2S, NH_3 and CFCs). The performance of these membranes will deteriorate severely if feed streams contain organic traces or other strongly adsorbing vapours.

Carbon membranes can be used in non-oxidising environments with temperatures in the range of 500-900 °C. A disadvantage of carbon membranes is that they are brittle and therefore difficult to package if the membrane surfaces become larger. Furthermore, the price of carbon membranes is still high and optimum manufacturing conditions still need to be determined (Delft et al., 2003).

3.5 Ceramic membranes

Ceramic membranes are constructed by combination of a metal with a non-metal in the form of an oxide, nitride or carbide. Ceramic membranes can be both, porous or dense.

Porous ceramic membranes generally have a two-layer structure: the separation membrane itself and a thicker, more porous ceramic supporting layer. The separation membrane is usually made of alumina, zirconia, titania, or silica. Depending on the components to be separated the selectivity can reach values up to 140. Hydrogen fluxes through the membrane are promising. Operating temperatures for the porous ceramic membranes are within the range 200-600 °C.

The development of porous membranes is at an early stage and most gas separation measurements have been made on samples of only a few square centimetres in surface area. Tubular samples of 20-90 cm have been fabricated but measurements under simulated operating conditions indicate that there are many issues to be resolved before this technology can be applied. One of these issues is limited stability in atmospheres containing steam. This stability may be increased by modifying silica membranes with methyl-groups (Delft et al., 2003).

In dense ceramic membranes, so-called proton conducting membranes (or proton exchange membranes), hydrogen is transported in the solid phase as ions (protons). Preferred materials are $SrCeO_{3-\delta}$ and $BaCeO_{3-\delta}$. The selectivity of this type of membranes is very high as basically only the hydrogen ions can migrate through the membrane material. Reported operating temperatures are in the range 600-900 °C. Some sources go as high as 1000 °C (Shah, Drnevich& Balachandran, 2000), but no experimental results at temperatures above 900 °C have been published. High temperatures (around 900°C) are required to achieve acceptable fluxes. Chemical stability in the presence of certain species (e.g., CO_2, H_2S) is a major concern. These membranes are still in an early stage of development.

Quite a separate category of (porous) ceramic membranes is formed by zeolites. These materials have channels inherent in their crystal structure and act as natural molecular sieves. However, achievable separation of small molecules is limited and fabrication of large thin zeolite plates still poses problems. They are presently at a very early stage of development.

Generally speaking, ceramic membranes still require considerable development and testing is mainly confined to bench scale level. Demonstration of feasibility of technology scale-up is necessary (Delft et al., 2003).

3.6 Glass membranes

Glass membranes are actually not very important for hydrogen separation. One of the reasons is their low selectivity. Glass membranes are porous. Depending on the pore size, they can be subdivided into micro porous (pores below 2 nm) and mesoporous (pores 2-5 nm). Micro porous membranes have higher selectivity yet lower fluxes. Both membrane types are usually produced from silica using the leaching manufacturing process. The temperature range where they can be used has an upper limit of 400-500 °C. Vycor glass membranes are commercially available.

3.7 Comparison/overview of the different membranes

Table 2 presents the properties of the most important membranes that can be used for hydrogen separation processes. A practical classification can be based on their operating temperatures:

- For temperatures up to 100 °C only dense polymer membranes can be used.
- For temperatures between 200 °C (or 300 °C) and 600 °C dense metallic or micro porous ceramic membranes could be used.
- For temperatures between (500 °C or) 600 °C and 900 °C porous carbon and dense ceramic membranes are suitable.

Table 2: *Properties of the relevant hydrogen selective membranes*

	Dense polymer	Micro porous ceramic	Dense metallic	Porous carbon	Dense ceramic
Temperature range	<100 °C	200-600 °C	300-600 °C	500-900 °C	600-900 °C
H_2 selectivity	low	5-139	>1000	4-20	>1000
H_2 flux (10^{-3} mol/m^{2}s) at dP=1 bar	low	60-300	60-300	10-200	6-80
Stability issues	Swelling, compaction, mechanical strength	Stability in H_2O	Phase transition	Brittle, oxidising	Stability in CO_2
Poisoning issues	HCl, SO_x, (CO_2)		H_2S, HCl, CO	Strong adsorbing vapours, organics	H_2S
Materials	Polymers	Silica, alumina, zirconia, titania, zeolites	Palladium alloy	Carbon	Proton conducting ceramics (mainly $SrCeO_{3-\delta}$, $BaCeO_{3-\delta}$)
Transport mechanism	Solution/ diffusion	Molecular sieving	Solution/ diffusion	Surface diffusion; molecular sieving	Solution/ diffusion (proton conduction)
Development status	Commercial by Air Products, Linde, BOC, Air Liquide	Prototype tubular silica membranes available up to 90 cm. Other materials only small samples (cm^2)	Commercial by Johnson Matthey; prototype membrane tubes available up to 60 cm	Small membrane modules commercial, mostly small samples (cm^2) available for testing	Small samples available for testing

4. MEMBRANE SYSTEM DESIGN

4.1 Introduction

Chapter 3 presented the membranes relevant to hydrogen separation and their most important properties. This chapter takes membranes a step further by providing an introduction into the design of actual membrane systems. A strong point of membranes is their versatility. A great number of variables can be chosen to arrive at an optimal design. At the same time, this versatility means it's very difficult to provide an in-depth membrane system design manual. Therefore, this chapter attempts not to provide a complete membrane system design overview, but merely some basic insights into the membrane design process. It is based on the design considerations presented in (Noble, 1995).

The first step in membrane system design is selecting a feed flow to be separated. The properties of this flow (temperature, pressure, composition), together with cost considerations, determine the membrane to be used, using the information provided in chapter 3. The next choice is what module shape is to be used. A module is the smallest practical unit containing a set membrane area and any supporting structures. For each membrane certain module shapes are commercially available. If another shape is desired, this will need to be designed and produced specifically for this application, leading to high cost. Apart from cost, other factors influencing the choice of a module shape are the operating pressure and fouling (mainly concentration polarisation).

Once the module shape is selected, the overall membrane system can be designed. In between the module and system level is the stage level. A stage is formed by one or more membrane modules assembled into an operating unit that provides a specific function different from any other membrane stages that may be utilized in the same process. System design is a matter of combining a number of stages in the optimal way.

This chapter starts with the transport equation used to calculate membrane fluxes. Section 4.3 presents the membrane module designs currently used. Section 4.4 shows the basics for a single stage membrane system. Some limitations of single stage systems can be overcome by using a multistage system. Several examples of multistage processes are presented in section 4.5. If (substantial) chemical reactions occur inside a membrane system it is called a membrane reactor. Some design considerations for membrane reactors are described in section 4.6. Finally, some practical issues, such as membrane deterioration are treated in section 4.7.

4.2 Calculating membrane permeate fluxes for gas separation

For given flows and membrane properties permeate fluxes of the various species through the membrane can be calculated using the following equation[1]:

$$J_x = \frac{P}{t}(p_{x,feed}^{n} - p_{x,permeate}^{n}) \tag{4.1}$$

where:

J_x	Permeate flux specie x (mole/(m^{2}s));
P	Permeability (mole/(msPa^n));
t	Membrane thickness (m);
$p_{x,feed}$	Partial pressure of specie x at feed side (Pa);
$p_{x,permeate}$	Partial pressure of specie x at permeate side (Pa);

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[1] There are more flux equations in use. In this report, only equation (4.1) is presented as it is mostly used to calculate fluxes; it is simple and illustrates the main factors influencing membrane fluxes.

n Partial pressure exponent (-).

The permeability P and the partial pressure exponent n in this equation depend on the transport mechanism assumed. The partial pressure exponent found is usually between 0.5 and 2. For porous membranes a value of 1 is mostly used in calculations since the main transport mechanisms are Knudsen diffusion for mesoporous membranes and molecular sieving for micro porous membranes. If n = 1 equation (4.1) is called Fick's law. For hydrogen diffusion through metals Sievert's law with n = 0.5 applies. This equation shows that an increase in membrane thickness results in a proportional decrease in flux. The last part of the above equation clearly shows that the driving force for gas permeation is the difference in partial pressures over the membrane: the larger this difference, the larger the fluxes. Partial pressures are defined as the mole fraction of the specie times the absolute pressure:

$$p_x = n_x \cdot p \tag{4.2}$$

Thus, the partial pressure differential can be increased by increasing the absolute pressure difference over the membrane as well as the relative difference in mole fractions of a specie over the membrane.

4.3 Current membrane module designs

The building block of a membrane system is called the module. All module types applied so far are based on two types of membrane configurations: flat and tubular. Module types based on flat membranes are the plate-and-frame and spiral-wound modules. Tubular-type membrane modules are subdivided into tubular, capillary and hollow fibre modules. The difference between the latter three is mainly based on their dimensions: tubular membranes are defined as having diameters larger than 10 mm, capillary membranes having diameters between 10 mm and 0.5 mm and hollow fibre membranes having diameters below 0.5 mm.

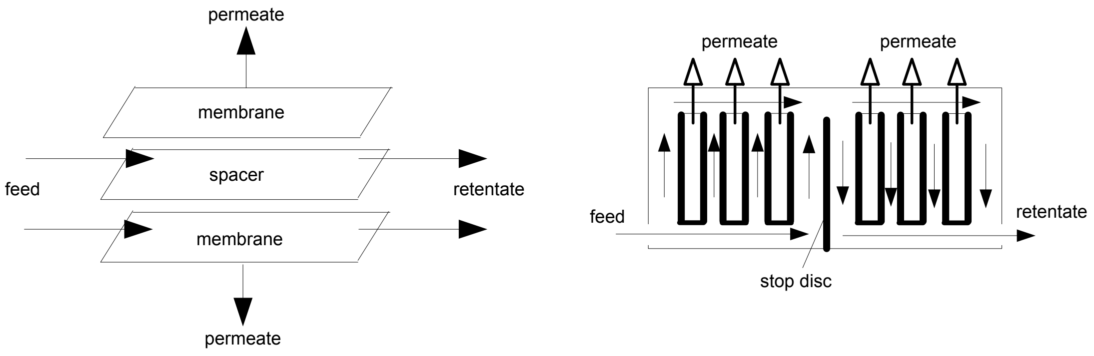

Figure 3: *Schematic drawings of plate-and-frame modules*

Plate-and-frame module

Plate-and-frame modules are the closest to common laboratory set-ups. They are constructed placing flat membranes parallel to each other, like in a sandwich (see Figure 3). The spacer plate separates the feed flows running alongside different membranes in the module. The stop disc in the right-hand figure is used to improve the flow pattern in order to use the membrane surface as efficiently as possible (to reduce so-called 'channelling', i.e., the tendency of the flow to move along a fixed pathway). The packing density (i.e., membrane surface per module volume) is around 100-400 m^2/m^3.

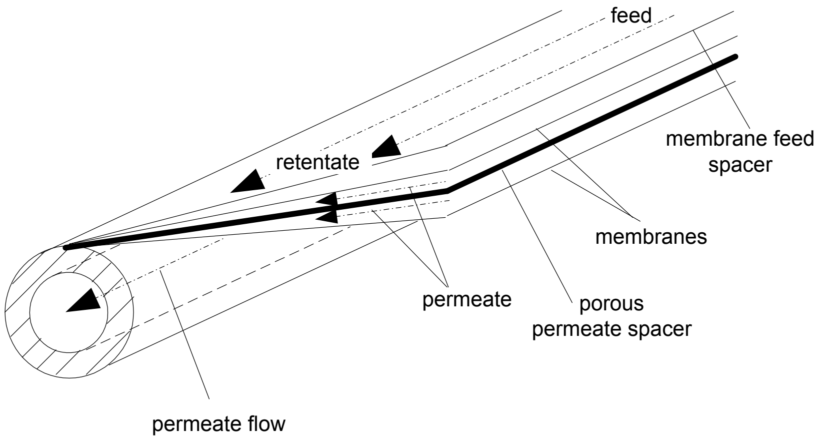

Figure 4: *Schematic drawing of a spiral-wound module*

Spiral-wound module

A spiral-wound module is a plate-and-frame system wrapped around a central pipe collecting the permeate (much like a sandwich roll, see Figure 4). The feed flow runs through the cylinder in axial direction, whereas the permeate runs in radial direction towards the centre of the cylinder. The packing density of spiral-wound modules is higher than the packing density of plate-and-frame modules (around 300-1000 m^2/m^3), but depends strongly on the channel height.

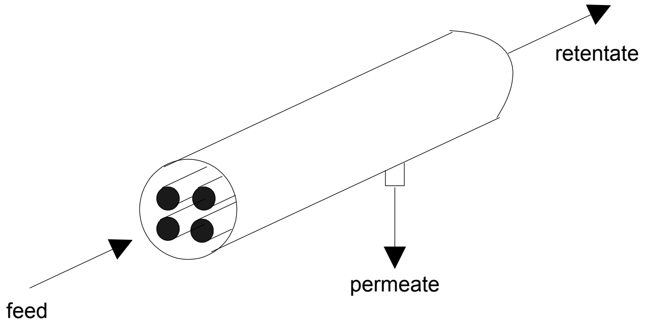

Figure 5: *Schematic picture of a tubular module*

Tubular module

Tubular membranes consist of a thin selective membrane layer deposited on the in- or outside of a tubular support with a diameter generally larger than 10 mm. The number of tubes put together in the module may vary from 4 to 8, but is not limited to this number (see Figure 5). The feed flows through the centre of the membrane tubes and the permeate crosses the membrane from the inside to the outside, flowing subsequently in the larger tube. The maximum packing density is around 300 m^2/m^3. Monolithic modules, constructed using a ceramic block and a number of membrane tubes inserted in the block, form a special category of tubular modules.

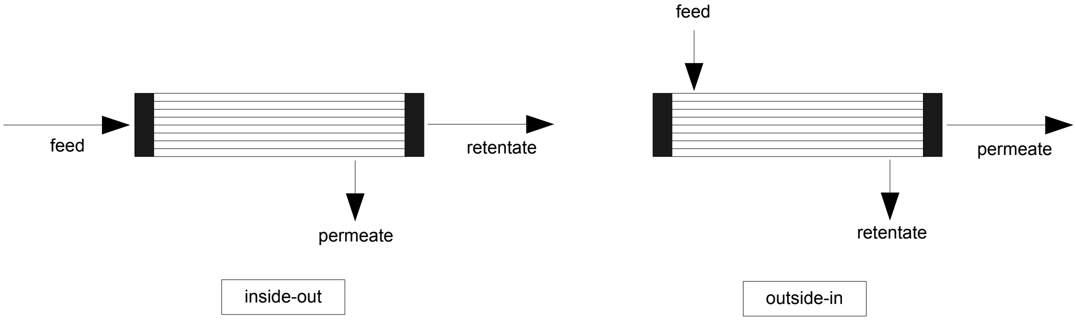

Figure 6: *Two schemes of capillary modules*

Capillary module

Figure 6 shows 2 types of capillary modules. The capillaries are self-supporting and bound together at the free ends (potted) with agents such as epoxy resins, polyurethanes, or silicone rubber. The feed flow can go through the bores of the capillaries, with the permeate exiting the membrane sideways (left scheme), but the feed can also run through the capillaries on the outside with the permeate exiting through the bores of the membrane. Packing densities to be attained are in the range 600-1200 m^2/m^3.

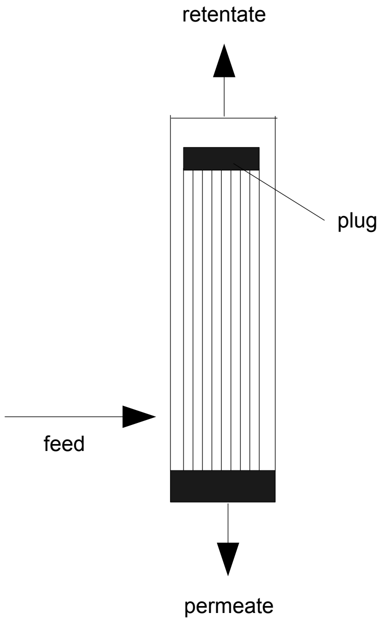

Figure 7: *Outside-in hollow fibre configuration for gas separation*

Hollow fibre module

The hollow fibre module is essentially the same as the capillary module, only the size of the tubes is smaller. Hollow fibres are essentially self-supporting and resistant to collapse in high-pressure and environmentally difficult situations (Paul, 1994). Of all the module types currently available, hollow fibre modules can reach the highest packing density of 30,000 m^2/m^3. Hollow fibre modules are preferably used when the feed stream is relatively clean. Because of the small bore diameter, pressure losses are relatively high. By selecting the 'outside-in' type pressure losses occurring inside the fibres can be reduced, and a high membrane area can be attained (see Figure 7).

The selection of a module shape depends on a number of factors, among which cost are very important. For each membrane certain module shapes are commercially available. If another shape is desired, it will need to be designed anew and produced, leading to high cost. For gas separation the module price depends to a large extent on the specific application (pressure, temperature, etc.). As the pressure vessel in which the membranes are located is the main determinant in total membrane unit cost for high temperature and pressure applications, under these circumstances a high packing density is desirable. This favours application of hollow fibre and to a lesser extent capillary and spiral wound modules. A disadvantage of thinner tubes is that the number of seals is relatively high. This will lead to extra cost, as cheaper sealing solutions, mainly resins, can not cope with high temperatures.

4.4 Single stage membrane processes

The simplest membrane processes are single stage membrane processes. A stage is formed by one or more membrane modules assembled into an operating unit that provides a specific function different from any other membrane stages that may be utilized in the same process.

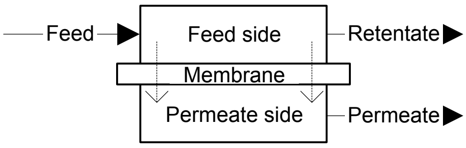

Figure 8: *Simple membrane set-up*

The basic membrane stage set-up is shown in Figure 8. Generally, membrane operations can be subdivided into dead-end and cross-flow operations. Dead-end operations occur if there is no retentate stream (the only exit of the feed side is the membrane). Although the recovery is high for this kind of operation, it is usually not preferred as non-permeating species in time become more abundant on the feed side, leading to so-called concentration polarisation. This means that the feed side concentration of the permeating specie decreases (in time), reducing the driving force and therewith the transport through the membrane.

Instead, cross-flow operations are preferred, i.e. configurations in which (some of) the flows run alongside the membrane. In this set up, deterioration of membrane flux in time is limited. In general, 4 cases of cross-flow operations are distinguished:

- co-current;
- counter-current;
- cross-flow with perfect permeate mixing;
- perfect mixing.

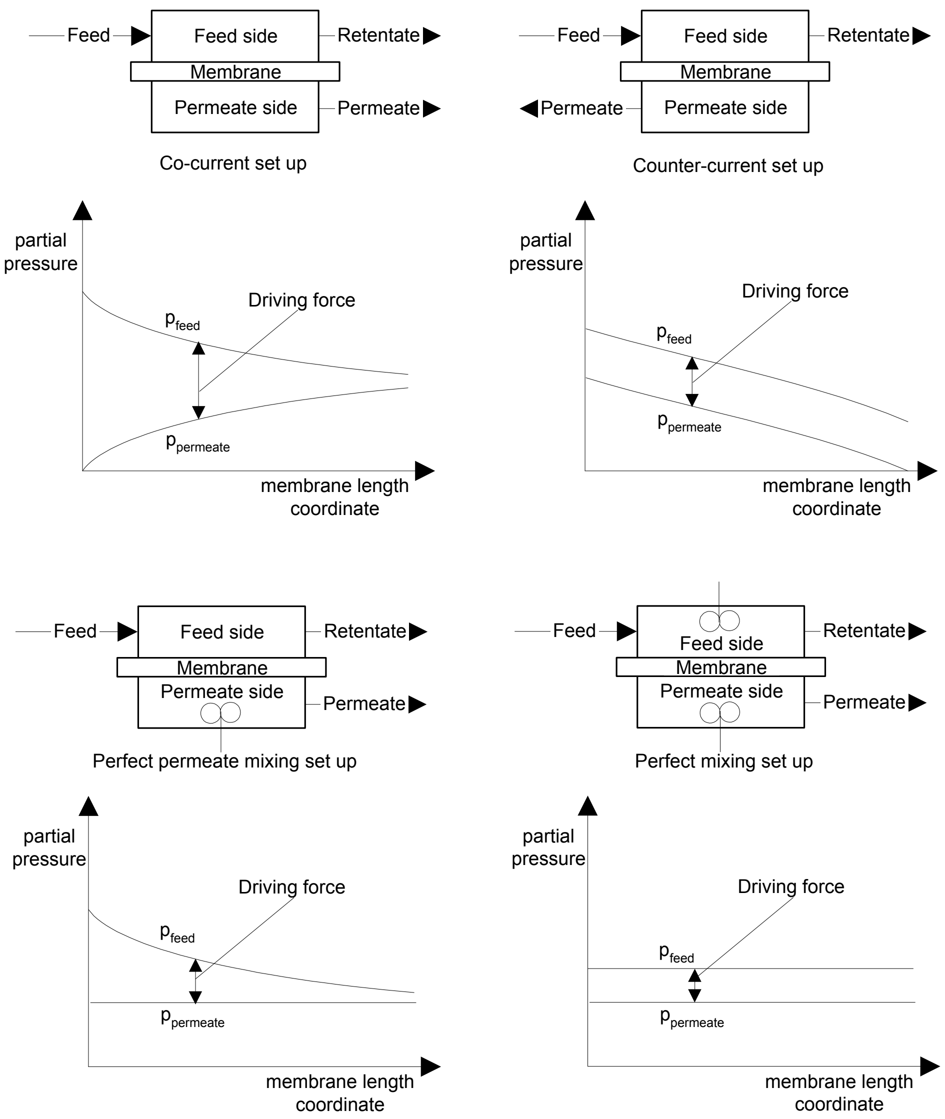

Figure 9: *Comparison co-current, counter-current, perfect permeate mixing and perfect mixing set up*

Co-current operation means that feed and the permeate (sweep) flows run in the same direction, whereas counter-current flow means that feed and permeate (sweep) flows run in opposite direction. In the perfect permeate mixing set up, the permeate is mixed, resulting in one permeate composition along the membrane length coordinate (see Figure 9). The perfect mixing set up results in one feed side composition and one permeate side composition.

In the co-current set up, the initial driving force is large, but it decreases as permeation takes place (see again Figure 9). If the membrane length is chosen large enough, the partial pressures on both sides will become (almost) equal. Therefore, the working efficiency of a membrane decreases with increasing membrane surface area. In the counter-current set up the permeate partial pressure decreases towards the (feed flow) exit of the module, resulting in a substantial driving force (partial pressure difference) even there. In the perfect permeate mixing set up, the permeate partial pressure is the same over the whole membrane length. The result is a retentate partial pressure approaching the permeate partial pressure, if the membrane surface area is chosen large enough. As the partial pressures on feed and permeate side are constant for each side of the membrane for the perfect mixing set up, this set up results in a constant driving force. Generally, the best membrane results are obtained using a counter-current flow set up, followed by cross-flow with permeate mixing and by co-current flow set up. Perfect mixing usually delivers the worst results (Mulder, 2000).

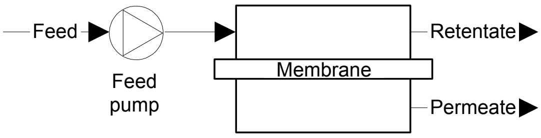

Figure 10: *Single stage membrane process with feed flow compression*

Apart from the flow operation, an endless number of variables can be adjusted to arrive at the optimal membrane set up. A few options will be presented here. It should be kept in mind that both the retentate and the permeate can be the desired flows. Figure 10 shows a membrane stage with feed compression. Feed compression will increase the pressure differential, and thus the driving force over the membrane. Consequently product recovery will increase. Compression in itself adds to the total plant cost, but reduced product loss results in smaller membrane plant size and lower cost. The net effect on cost will depend on the specific situation.

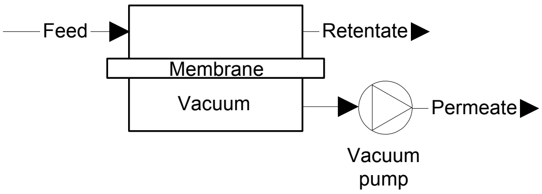

Figure 11: *Single stage membrane process with permeate vacuum*

Another way to increase the pressure differential over the membrane is to decrease the permeate pressure, possible down to vacuum. This set up is shown in Figure 11. An advantage of this set up over feed flow compression is that the flow to be compressed by the vacuum pump is generally smaller than the feed flow.

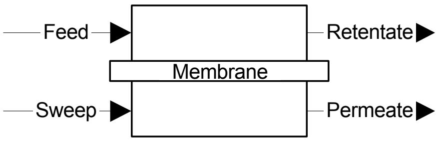

Figure 12: *Single stage process with permeate dilution by means of sweep flow*

As shown in section 4.2, the partial pressure differential over the membrane can be influenced by increasing the absolute pressure differential over the membrane (e.g., by feed compression or permeate vacuum), but also by changing the compositions of feed and permeate flow. Figure 12 shows one way of achieving just this, by diluting the permeate with a sweep flow. Again, the improved membrane transport and thus a smaller membrane unit may offset the extra cost of providing a sweep flow (e.g., steam production).

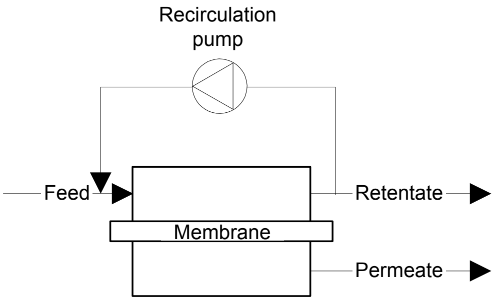

Figure 13: *Single stage membrane process with recycle*

Furthermore, the membrane retentate or permeate flows can also be partly recycled (see Figure 13). This provides a more flexible set up and can enhance product recovery. Especially with polluted flows and concentration polarisation this can be a good option.

Noble and Stern come to the following generalizations for single-stage membrane processes:

- Membrane area requirements are reduced and product recoveries are increased as the pressure differential over the membrane increases;
- The absolute permeate pressure (or pressure ratio) is also important. Higher pressure ratios lead to improved separation performance. Pressure differential alone does not define membrane performance;
- Increasing membrane area leads to a purer residue but a less pure permeate;
- Product recoveries tend to drop rapidly as the purity requirement is increased.

4.5 Multistage membrane processes

To improve membrane system performance, multistage membrane systems can be built. These usually require additional equipment but the costs are often small relative to the gains from the process improvements (Noble, 1995).

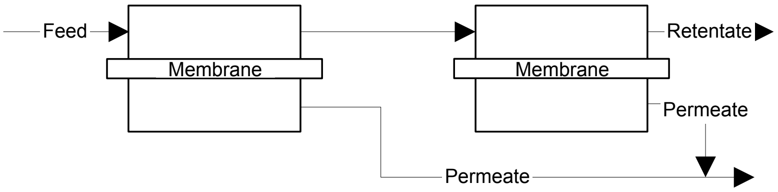

Figure 14: *Two-stage membrane process as simple split up of single stage process*

Even a simple split up of a single membrane stage into two stages may prove advantageous under certain circumstances. Although the final permeate flow in Figure 14 will not be any different from the permeate flow of the single stage system before the split up, the separate permeate flows of both membrane units will be different (and can be quite different). This difference can be used if the streams are used for different purposes.

Most multistage membrane systems incorporate some sort of recycle to enhance product separation and recovery. Such designs are easy to implement from a membrane standpoint, but always require compression for the recycle stream. Gas compression is expensive, but recycling generally improves overall process efficiency (Noble, 1995).

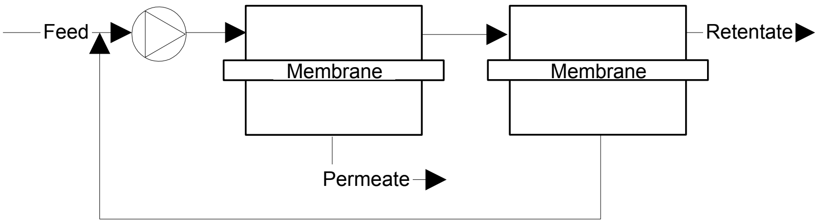

Figure 15: *Two-stage membrane process with permeate recycle*

The process shown in Figure 15 can be used to enhance product recovery. The first membrane unit produces a permeate with the desired product purity, yet the retentate still contains a relatively large fraction of the desired product. The second membrane unit is used to reclaim the main part of this desired product from the retentate flow. Since the purity of the permeate of this second membrane unit is considered too low, it is recycled to the feed flow.

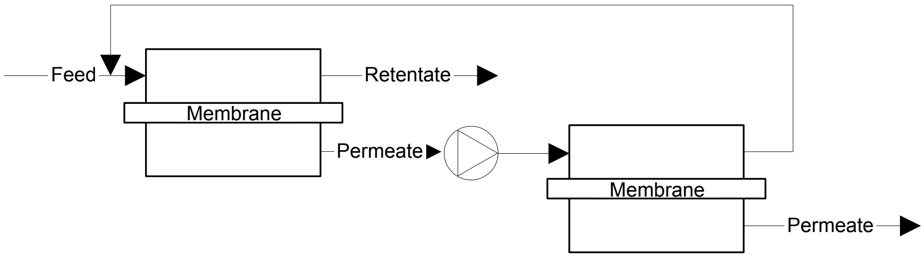

Figure 16: *Two-stage membrane process with cascade*

Another popular multistage membrane set up is a so-called cascade (Figure 16). This option is particularly useful if the first stage can't produce the desired permeate purity. The permeate is then passed on to a second membrane unit (after it has been recompressed if required). The retentate of this second unit can be recycled to the feed stream to enhance product recovery.

These are only a few of the membrane systems possible applying two membrane stages. It is not hard to imagine that many more membrane systems can be conceived by combining even more membrane stages. This versatility of membrane systems adds to their attractiveness for various industrial applications.

4.6 Membrane reactors

An important advantage of membranes derives from the ability to selectively permeate species taking place in equilibrium reactions. If no membranes are applied, temperatures are adjusted and/or reactant species are added to shift these reactions to the product side. Both options are often not favourable from a system efficiency point of view. Membranes offer the opportunity to selectively take away reaction products, thereby shifting the equilibrium to the product side.
If chemical reactions are carried out (on a considerable scale) in a membrane module, the system is called a membrane reactor. The fact that reactions occur in membrane modules complicates the module design. The reactions may result in substantial composition changes, influencing membrane operation through changes in partial pressures or formation/depletion of contaminants.

For reactions to occur in a membrane module, catalysts may be needed. These catalysts will need to be accommodated inside the membrane reactor. Three types of arrangements are found to accomplish this (Mulder, 2000):

- catalyst placed inside the feed stream;
- catalyst placed in a membrane top layer;
- catalyst placed inside the membrane itself.

The most simple catalyst arrangement is the first option: placed inside the feed stream. This arrangement is easy to prepare and operate. If needed, the catalyst can also easily be replaced. If the catalyst is placed in a membrane top layer or inside the membrane itself, replacing the catalyst involved usually means replacing the complete membrane.

The most important issue of a membrane reactor is likely to be heat balancing. Reactions usually have temperature effects, either endothermic or exothermic. If several reactions occur at the same time they may roughly balance each other thermally. However, it is more probable that there will be a need for heat exchange. This can place large constraints on membrane reactor design. For example, in case of a methane reforming membrane reactor, a large heat influx is required, since the reforming reaction is strongly endothermic. To introduce this heat at the places where the reaction has to occur (near the membrane where the hydrogen needs to be taken away) is a complicated task.

The potential applications of membrane reactors are numerous, but commercial applications are hindered by practical limitations such as low separation factors, leakage at higher temperatures, poisoning of catalysts and mass transfer limitations (Mulder, 2000).

4.7 Some practical issues

Membrane performance generally decreases with time. This phenomenon can be caused by concentration polarisation and fouling. Concentration polarisation occurs because of limited permeation of certain species. These species will become higher in concentration directly adjacent to the membrane reducing permeate transport. The size of this effect depends on the type of species used and the flow set up (see section 4.4). Concentration polarisation is usually not a very severe problem for gas separation membranes. If concentration polarisation does occur, turbulent flow can be promoted in the gas flow directly adjacent to the membrane to minimize the negative effect. By doing so, a better mix of the concentrated layer with the feed flow will be obtained. Decrease in flux due to concentration polarisation is generally constant over time.

Fouling is said to occur when species adsorb to the membrane surface (also inside the pores), limiting or even blocking permeation. Notable examples of species fouling membranes are sulphur containing species such as H_2S and SO_2. To mitigate the effects of fouling, membranes can be cleaned by heating and purging with non-adsorbing gases. Small particles can best be removed from the feed flow using a filter.

Membrane deterioration may also be caused by compaction, i.e. a reduction of pore size, because of pressurization. This phenomenon occurs with polymer membranes and is usually irreversible: most often the pore size doesn't return to its original value when pressure is decreased.

In making choices to obtain the optimal design, other practical considerations come into play. One of these is the effect of thermal stresses on the structural integrity. If temperature variations occur, several parts of the system may experience different degrees of expansion. If there is no room to accommodate these differences in expansion, the system can be seriously damaged.

Furthermore, the pressure drop over a membrane unit (not the membrane itself) is directly proportional to the module length. To reduce the pressure drop, it would be advantageous to apply shorter modules. However, shorter modules will lead to more seals.

Another issue to be considered is the ease in starting up and shutting down of the unit. A system design needs to accommodate these effects.

5. CONCLUSIONS

Although there is certainly competition from other separation technologies, such as pressure swing adsorption (PSA) and cryogenic separation, membrane systems for gas separation have enjoyed growing interest in the last half century. Currently the number of hydrogen selective membrane applications is still limited to two, and both applications are not in critical parts of the process. These two are hydrogen recovery from off-gases in the ammonia industry and production of pure hydrogen in the electronics industry. Research is going on, intended to apply hydrogen selective membranes in more critical parts of the process.

There are several hydrogen selective membranes, each with their own operating ranges, in terms of temperatures and flow compositions. The properties of the feed flow to be separated are therefore a starting point to select a suitable membrane. For temperatures below 100 °C, only dense polymer membranes can be used; in the temperature range between 200 and 600 °C, dense metallic or micro porous ceramic membranes can be used; and in the temperature range between 600 °C and 900 °C, porous carbon and dense ceramic membranes are most suitable. Applicability of these membranes is also limited by sensitivity towards certain species and cost. Moreover, the development status of these membranes varies.

Once the membrane type is selected, the membrane module can be chosen or designed taking into account considerations such as manufacturability, maintainability, operability, efficiency, membrane deterioration, and costs.
Currently five module types exist, plate-and-frame and spiral-wound modules, based on flat membranes, and tubular, capillary and hollow-fibre modules, based on tubular membrane geometries. Generally, for gas separation the module price depends to a large extent on the specific application (feed pressure, temperature, etc.). Especially for high temperature and pressure applications a high packing density is desirable. This favours application of hollow-fibre and to a lesser extent capillary and spiral wound modules.

Modules are combined into stages. The options for membrane system layout are virtually endless, as stages can be combined in various ways, and processes can be changed by adding compressors and recycles.

A design also needs to accommodate occasional cleaning/replacement and possibly carrying out of chemical reactions. If chemical reactions are carried out on a large scale, heat management issues may complicate membrane operations. Moreover catalysts may need to be incorporated into the membrane systems.

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