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New Advances in Membrane Technology

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1. Introduction

Research into the use of membrane-based processes in the industry is an interesting area for modern membrane science and technology. The main purpose in this chapter is to describe and discuss a few selected, well recognized and also promising aspects of membrane usage in the industry with the focus on energy conversion, environmental protection and process intensification in this broad field.

2. Membranes for Energy Conversion

The energy strategy is changing all over the world. There are different reasons for this: Fossil fuels will become rare in less than 50 years; more than 64% of the current petroleum reserve is located in the Middle East, while less than 14% is available in Europe, USA and the former USSR region together. Energy independence is a security issue. As a consequence different low emission renewable energy technologies are being implemented, favoring the use of bio-fuels and hydrogen to power our future. At the same time the modernization of conventional power plants and refineries is being stimulated to reduce their emission of CO_2 in a transition period when petroleum and coal are still the predominant fuel sources. In all these new technologies and transition steps, membranes have a huge opportunity to become a key player.

2.1 Fuel Cells

Fuel cells are the main zero emission energy converters fed with hydrogen or renewable fuels like methanol and ethanol to power vehicles, portable devices or to supply electricity to buildings. Various proton-conducting polymer electrolyte materials have been investigated for high temperature operation. Two categories of membranes can be proposed, depending on whether water is required for proton conduction or is not necessary. Polymer electrolytes involving water molecules in the proton mobility mechanism (e.g., perfluorosulfonic membranes) need humidification to maintain suitable conductivity characteristics. The amount of humidification may vary depending on the operating temperature and membrane properties; it influences the size and complexity of the device. Some other electrolytes do not necessarily involve water molecules in the mechanism of

proton conduction; these systems do not strictly need humidification. Yet, there are some drawbacks related to the short-term stability of such systems: phosphoric acid leakage from the membrane during operation, poor extension of the three-phase reaction zone inside the electrodes due to the absence of a proper ionomer, and reduced conductivity levels for inorganic proton conductors (Tchicaya-Bouckary et al., 2002).

These problems have decreased the perspectives of utilization of water-free protonic electrolytes in low temperature fuel cells. Alternatively, composite perfluorosulfonic membranes containing different types of inorganic fillers such as hygroscopic oxides, surface modified oxides, zeolites, inorganic proton conductors and so on have shown an increased conductivity with respect to the bare perfluorosulfonic membranes at high temperature and fuel cell operation up to about 150°C has been demonstrated. Such an effect is mainly due to the water retention capability of the filler (Kreuer, 2001).

Fuel cell operation at elevated temperatures can limit the effects of electrode poisoning by adsorbed CO molecules, increase both methanol oxidation and oxygen reduction kinetics and simplify water and thermal management. High temperature operation can reduce the complexity of the reforming reactor employed; the temperature range 130 to 150°C is ideal for application of these systems in electric vehicles and for distributed power generation (Jung et al., 2003).

The presence of hygroscopic inorganic oxides inside the composite membrane, besides extending the operation of perfluorosulfonic membranes (e.g., Nafion) in the high temperature range, reduces the cross-over effects by increasing the ''tortuosity factor'' in the permeation path. Such effects are particularly serious at high temperature in fuel cell systems. Presently, these membranes appear to operate better at high pressure since this allows one to maintain a suitable content of liquid water inside the assembly or to facilitate water condensation in the pores. In fuel cell devices, cathode operation at high pressure reduces system efficiency because of power consumption by the air compressor; whereas, less remarkable, is the power loss for the liquid pump at the anode. Although, significant progress has been achieved in the last few years on the development of composite membrane-based systems, the high-pressure requirement is actually the main feature limiting large application of such composite electrolytes at temperatures above 100°C (Arico et al., 2003).

Two strategies have been pursued in the study of the perfluorosulfonic composite membranes. A series of composite membranes based on recast Nafionionomer containing different inorganic nanoparticle fillers (SiO$_2$, phosphotungstic acid-impregnated SiO$_2$, ZrO$_2$, Al$_2$O$_3$) mainly varying in their acid–base characteristics has been prepared and investigated in fuel cell devices. In this series of membranes water was used as solvent. In another series of membranes, only one inorganic filler (TiO$_2$) was selected; this was tailored in terms of morphology and surface chemistry and was used for preparation of composite membranes prepared by casting Nafion ionomer in the presence of dimethyl sulfoxide (DMSO).

2.2 Hydrogen Separation

Hydrogen is the lightest element in the periodic table and is primarily used as a chemical building block in a large number of chemical processes. Currently, about 96% of hydrogen is produced from fossil fuels with close to 48% from natural gas (methane), ~30% from petroleum feedstock (oil) and ~18%from coal. Only about 4%of hydrogen is produced by electrolysis although this is almost certain to increase in the future. The major use of

hydrogen, close to 50% of that produced, is in ammonia synthesis, followed by refinery use and methanol synthesis. Only a very small fraction is used as a fuel although this will undoubtedly increase in the near future as we enter the era of the hydrogen economy (Gryaznov, 2000).

Membranes for hydrogen separation are available for different temperature ranges. Two classes of inorganic membranes for hydrogen separation are treated: palladium membranes (temperature 300-450oC) and mixed proton and electron conductive materials (above 600oC). For temperatures up to 550oC molecular sieve membranes based on silica or zeolite are the state-of-the-art (Duke et al., 2006). For temperatures higher than 250oC polymer membranes cannot compete but for the low temperature range they have some advantages, being easy to produce and manufacture in modules on a large scale. A potential application for this temperature range is the recovery of hydrogen from fuel gas and platform off-gas. Glassy polymers with high temperature stability like some polyimides are suitable for membranes for preferential hydrogen transport (Shishatskiy, 2006).

Steam reforming of natural gas is by far the most common process used for the production of hydrogen. In steam reforming, methane is mixed with steam and the catalytic reaction is carried out at high pressure (e.g., 30-40bar) and high temperature (700-900oC). Because the reaction is controlled by thermodynamic equilibrium, in order to increase the overall conversion of the process, shift reactors (high and low temperature) are used to increase the hydrogen conversion, followed by a preferential oxidation reactor (PreOx) and hydrogen separator.

Unfortunately, the by-product of the reaction is the greenhouse gas CO_2, which could not and should not be exhausted to the atmosphere and needs to be treated. A membrane reactor can increase the overall conversion of a thermodynamic equilibrium-controlled reaction by continuously removing one or more of the reaction products during the reaction. Therefore, it is especially suited for carrying out the steam reforming reaction (Klette & Bredesen, 2005).

Metallic membranes, particularly, Pd and Pd/alloy membranes supported on porous metal, are well suited for the steam-reforming application. Both metallic membrane and porous support are chemically, mechanically and thermally stable at high temperatures and pressures. Composite membranes supported on porous metal have the advantage over stand-alone thin films because a thin membrane layer can be made since the porous support provides the necessary mechanical strength required for high pressure applications.

The persisting perception that palladium is too expensive to be economically feasible for large scale applications is misleading. Since the reduction in thickness of a composite Pd and Pd/alloy membrane to less than 5mm or thinner is feasible the quantity of palladium used is so small that its cost becomes an insignificant fraction of the total membrane assembly cost. However, the cost of the support may become significant and may play a considerably more important role in making composite Pd and Pd/alloy membranes economically viable for large scale industrial applications. On the other hand, the cost of the support may become much lower than the current price when large quantities are purchased, thereby making the process more competitive with the conventional steam reforming processes. In addition, in order to get the maximum economic and operational benefits, composite Pd and Pd/alloy membrane reactors should be considered.

The known hydrogen-permeable dense ceramic materials are oxides that are mixed proton–electron conductors. Proton transport at high temperatures is fast, but thermodynamics

speaks against a high concentration of protons in the materials at high temperatures. Combinations of both high protonic and electronic conductivity appear to be remarkably rare. Materials' chemical and thermal stability, mechanical strength, and the ceramic engineering are important to make dense, thin membranes on porous supporting substrates – all needed to arrive at long-lived high-performance membranes for hydrogen separation at high temperatures.

2.3 CO_2 Capture and Power Generator

Approximately one third of the main anthropogenic sources of CO_2 originate from power generation. The growing acceptance that this emission causes an increase in the global temperature with enormous potential consequences, has led to efforts to develop technology for CO_2 mitigation. This may be achieved by following simultaneously several strategies such as:

1. Improving energy efficiency
2. Changing to low carbon fuels, or CO_2 neutral or non-emitting power generation and chemical production routes,
3. Developing CO_2 capture and storage technology.

Membranes may play an important role in the different technologies for CO_2 mitigation listed above (Powell & Qiao, 2006).

Traditional CO_2 separation is accomplished by physical and chemical absorption, adsorption, cryogenic distillation and membrane technologies. Different approaches for material development for membranes with preferential CO_2 transport include functionalized polymers and polymer composites containing polar ether oxygens (Lin & Freeman, 2005) and/or amine groups. An approach which is under investigation by different groups is the use of polymers with ethylene oxide segments. Recently, highly branched, cross-linked poly (ethylene oxide) was reported with particularly high selectivity (up to 30) for CO_2/H_2. Commercially available membranes for CO_2 separation are polymeric and are operated at close to ambient temperatures. Selectivity for CO_2/CH_4, CO_2/N_2 and CO_2/H_2 is typically well below 50 and permeance fairly low, which is a major drawback for this type of membrane. Development of hybrid membranes (polymers containing inorganic materials) may give improvements. However, due to the better thermal stability, and typically better selectivity and permeance, inorganic membranes will give new possibilities of integration in power cycles that could result in higher efficiency and reduction of total cost for CO_2 capture.

It has been shown that inorganic membranes can be integrated in different fossil fuel-based power cycles with CO_2 capture. Studies comparing the power cycle efficiency show that a penalty of only 5-8% for CO_2 capture is possible by membrane integration. Some state-of-the-art membranes already demonstrate sufficient flux and selectivity to give cost-effective CO_2 capture solutions. The properties of current membranes appear, however, critically dependent on stringent control of all stages in advanced production processes. Consequently, fabrication is difficult, and significant work is necessary to realize economically viable large scale production of membrane modules. Several companies are currently involved in such efforts and in validating performance under real operating conditions (Lin et al., 2006).

2.4 Power Generation by Pressure Retarded Osmosis

The shrinking reserves of fossil fuels and the increasing energy demand due to the development of third world countries are only some reasons for the urgent need to search for alternative emission free energy sources. Solar and wind power are already well established and part of our day to day life. The ocean as an energy source has not yet been developed to a commercial level but it represents a renewable energy source with a high potential. Ocean energy sources were accessed during the energy crises after 1973 with regard to their energy density and potential power. Sources considered were ocean waves, ocean currents, thermal gradient, tides and salinity gradient. Salinity gradient power systems include Reversed Electrodialysis and Osmotic Power, the latter using Pressure Retarded Osmosis (PRO). A comparison of these two processes has been published recently (Post et al., 2007).

Osmotic Power using pressure retarded osmosis is one of the most promising renewable ocean energy sources. It represents a huge potential and can make a significant contribution not only to satisfying the global energy demand but also to reducing the environmental impact of power production.

Scientists have known of this energy source for more than 30 years but, due to lack of effective membranes, the key part of an Osmotic Power plant, not much effort has been made to establish this type of energy. Osmotic Power using the PRO process has the potential to be a huge energy resource. It produces no CO_2 or other emissions that may interfere with the global climate and is a predictable energy form compared to solar or wind power. Statkraft, the leading power utility and electricity provider in Norway, started their research on Osmotic Power in 1997 together with the Norwegian research institute SINTEF.

In order to establish this form of green energy, the membrane, the heart of the process needs further improvement. The break even value for the membrane performance is 5W/m², so there is still a need to improve the design of the membrane and the process of industrializing the technology (Jones, & Rowley, 2003).

The performance of cellulose acetate (CA) membrane and the thin film composite (TFC) membrane has been tested, reaching 3.7W/m² for the best ones. The target performance for commercialization is 5W/m². The achievements from the research to date show that the realization of PRO is getting closer. Although there is still need for further improvement of the membrane performance, no obstacles have been identified that should prevent PRO from becoming a large-scale power technology within a few years. From the results shown earlier it can be concluded that asymmetric CA membranes have been developed close to the maximum performance of this polymer. The target of 5W/m² can probably not be reached with CA membranes, but the transfer of this technology to hollow fibers can still imply interesting improvements. The TFC membranes made by interfacial polymerization have the potential to reach the designated performance of 5W/m².

3. Membranes for Environmental Protections

Water supply and environmental protection are two important challenges of the current century. Due to increase in the world population and limited sources of the water, more efficient processes for water processing and reuse are needed. Also, daily discharge of large amounts of wastewater, domestic and industrial effluents and other gaseous and liquid pollutants to the environment has been made the earth more and more unsafe for living.

More expensive and energy and time consuming processes for water and wastewater conditioning such as multistage flash evaporation and biological activated sludge processes are now going out of date and new and more effective processes such as reverse osmosis (RO), ultra filtration (UF) and membrane bio-reactors (MBR) are replaced. In this section, the application of the new membrane processes for wastewater and environmental protection are discussed (Judd & Jefferson, 2003).

3.1 Wastewater Treatment

Almost every manufacturing industry (automobiles, food, steel, textiles, animal handling and processing, etc) and service establishment (hotels, transportation, etc.) generates large quantities of wastewater daily. Industry accounts for about a quarter of all water consumption, and there is hardly any industry that does not use large volumes of water. The need for stringent pollution control (and legislation) provides tremendous opportunities for membrane technology in all aspects of pollution control, from end–of-pipe treatment to prevention and reduction of wastes.

There are two approaches to wastewater treatment, depending on (1) if the permeate is to be reused, e.g. alkaline/acid cleaning baths, electrocoat paint, water, or, (2) if the permeate is to be disposed of and objective is to reduce the volume of solids, e.g., machining operations, food wastes, metal plating. However, the physicochemical properties of wastes vary widely, even within the same industry and sometimes within the same plant at different times of the year. Wastewater treatment requires more extensive testing than most industrial membrane applications to account for possible feed-stream variations, pretreatment options, cleaning problems, and issues related to recycling or disposal of permeate and retentate (Cheryan, 1998).

3.1.1 Solid Membranes

Solid membranes play an important role in wastewater treatment. As they are the oldest kind of industrial membranes, they have been employed in many industrial applications.

3.1.1.1 Oily Wastewater

Oily wastes are generated in a wide variety of industries such as metalworking, vegetable and food processing, transportation, textiles, laundries, chemicals, etc. They are grouped as three broad categories: free oil, unstable oil/water emulsions, and highly stable oil/water emulsions. Free oil can be readily removed by mechanical separation devices that use gravitational forces as the driving force. Unstable oil/water emulsions can be mechanically or chemically broken and then gravitationally separated. However, stable emulsions, particularly water-soluble oily wastes, require more sophisticated treatment to meet today's effluent standards.

Using UF to recover the oil component and allow safe discharge of the water makes good economic sense, and this application covers a wide volume range. In large, automated machining operations such as automobile plants, steel rolling mills, and wire mills, a central ultrafiltration system may process up to 100,000gal/day of waste emulsion. These are relatively sophisticated plants that operate continuously using several ultrafiltration feed-and-bleed stages in series. At the other end of the scale are very small systems dedicated to single machines, which process only a few gallons of emulsion per hour. The principal

economic driver for users of small systems is the avoided cost of waste hauling. For larger systems the value of the recovered oil and associated chemicals can be important. In both cases, tubular or capillary hollow fiber modules are generally used because of the high fouling potential and very variable composition of emulsified oils. A flow diagram of an ultrafiltration system used to treat large machine oil emulsions is shown in Figure 1. The dilute, used emulsion is filtered to remove metal cuttings and is then circulated through a feed-and-bleed ultrafiltration system, producing a concentrated emulsion for reuse and a dilute filtrate that can be discharged or reused (Baker, 2004).
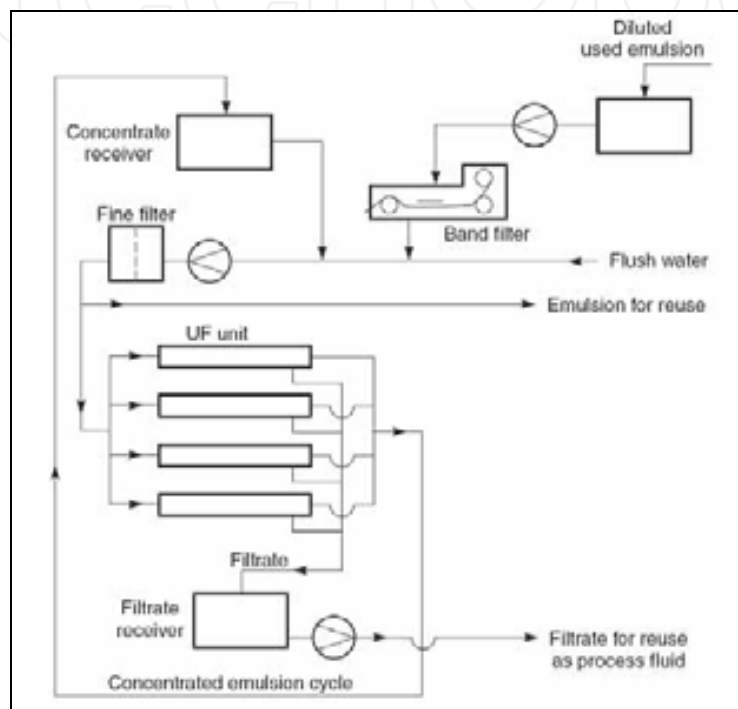

Fig. 1. Flow diagram of a UF unit used to concentrate a dilute oil emulsion (Baker, 2004).

3.1.1.2 BOD and COD Reduction

The presence of organic materials in wastewaters can result in many problems. The appropriate indices for showing the amount of organics in water are the chemical oxygen demand (COD) and the biological oxygen demand (BOD). Membrane processes have received considerable attention for the separation and concentration of inorganics and organics from various wastewaters. Membrane processes have been combined with or substituted for traditional advanced treatment technologies such as biological treatment, adsorption, stripping, oxidation, and incineration. The membrane processes can be used to concentrate and purify simultaneously wastewater containing both inorganics and organics and produce a 20 to 50 fold decrease in waste volume that must be treated with other processes.

The development of low-pressure processes has made RO an attractive alternative for the treatment of aqueous wastes since these offer high fluxes and solute separations and can operate over wide temperature and pH ranges. RO processes for wastewater treatment have been applied to the chemical, textile, petrochemical, electrochemical, pulp and paper, and

food industries as well as for the treatment of municipal wastewater (Madaeni & Mansourpanah, 2003).

Both UF and RO membranes used for COD and BOD reduction in wastewaters depend on the size of the organic molecules. When both high and low molecular weight organics are present in wastewater, it is customary to use UF as a pretreatment for RO process. This combination allows removing more than 90% and in some cases more than 99% of TOC from wastewater. The shortcoming of this combination is the need of high pressure operation (20-80bar) for RO systems, but it has the benefit of high rejections for even concentrated wastes. Recently, application of nano filtration (NF) instead of the above combination has been developed. This system does not suffer from high pressure operations as RO systems and usually works with a pressure lower than 20bar, but the percent of rejection is nearly 50% of the RO system and is suitable for low contaminated wastewaters (COD<400 ppm) (Viero et al., 2002).

3.1.1.3 Heavy Metal Ion Removal

Heavy metals constitute a major portion of the contaminants in chemical effluents that cannot be degraded or destroyed. Heavy metals are dangerous due to bioaccumulation. In water bodies, they accumulate in sediment and organisms from where they may transfer into the food chain. Due to their hazard to human health, lead, arsenic, cadmium and mercury are targeted by international environmental legislation (Landaburu-Aguirre et al., 2006). Although solvent extraction is frequently employed for removal of selected species from aqueous solutions, this technology suffers from a requisite maintenance of a large inventory of an organic solvent that is often flammable, toxic or otherwise hazardous. Other traditional methods for elimination, concentration and/or recovery of heavy metals are precipitation, ion exchange (IX), electrodeposition, crystallization, evaporation, etc. In the majority of cases, the ultimate objective of the process is not the recovery of the metal but rather its elimination. However, recovery of heavy metals allows their later re-use and thus provides further economic and environmental benefits by contributing to reduced disposal costs and raw material requirements.

Membrane processes provide a viable alternative for heavy metal recovery, as they can achieve high permeate fluxes and high rejection coefficients with low energy costs and under mild conditions. In addition, using membrane technology separation can be carried out continuously and membrane processes can easily be combined with other separation processes (hybrid processing). Nearly all kinds of membranes (UF, NF, RO and IX) have been employed for heavy metal ion removal from wastewaters but RO and NF are more common than the others (Abu Qdaisa & Moussab, 2004).

3. 1. 2 Liquid Membranes

For more than 30 years, liquid membranes have been in focus of research. Since diffusivities in liquids in comparison with solids are higher by several orders of magnitude, enhanced permeabilities of liquid in comparison with solid membranes can be expected (Krull et al., 2008). Recently, liquid pertraction or liquid membranes appeared as a new and prospective separation method. Due to its advantages over solid membranes and liquid-liquid extraction, liquid pertraction attracted the attention of many scientists and engineers.

Liquid pertraction explores a very simple idea: two homogeneous, completely miscible liquids, which may be referred to as *donor* solution, and an *acceptor* solution are spatially separated by a third liquid, immiscible and practically insoluble in the former two liquids--the *membrane* phase. Due to the favorable thermodynamic conditions created at the interface between the donor solution and the organic membrane, some components are extracted from the donor solution and transported into the membrane liquid. Simultaneously, at the second interface, conditions are created, which favor the reverse transport, i.e., the extraction of the above-mentioned components from the membrane liquid and their accumulation in the acceptor solution.

Liquid membranes (LMs) have two considerable advantages over solid membranes: as is known, molecular diffusion in the liquids (except in super-viscous ones) is, by several orders of magnitude faster than that in solids. Furthermore, in some pertraction methods the molecular diffusion in the liquid membrane is replaced by eddy diffusion, which intensifies the transfer process. Hence, it may be stated that solid membranes, even those of submicron thickness, cannot compete with liquid membranes with respect to transfer intensity. As a general rule, polymer membranes are less selective than liquid ones.

Wastewater treatment using LM is a new insight in membrane technology. All of the three kinds of liquid membranes (emulsion, bulk and supported liquid membranes) have their specific applications in wastewater treatment. Among the various activities in this field, the most important ones are:

− Removal of phenol from concentrated phenolic wastewater (up to 50000 ppm) by ELM (Kargari et al., 2002; Kargari et al., 2003d; Kargari et al., 2005b).
− Removal of iodine from highly concentrated aqueous media (up to 2000 ppm) by BLM (Nabieyan et al., 2007; Kaghazchi et al., 2009).
− Removal of cadmium ion from aqueous media (up to 100 ppm) by SLM (Nabavinia et al., 2009).
− Removal of chromium ion from aqueous solution by BLM (Rezaei et al., 2004).
− Removal of the gold ion from aqueous media, selectively (up to 110 ppm) by ELM (Kargari et al., 2003a-c; Kargari et al., 2004a-e; Kargari et al., 2005a; Kargari et al., 2006a-c; Mohammadi et al., 2008).
− Removal of bio-organic materials from aqueous media by ELM (Kaghazchi et al., 2006).

3.2. Nuclear Waste Treatment

The nuclear industry generates a broad spectrum of low and intermediate level liquid radioactive wastes (LRWs). These liquid wastes may be produced continuously or in batches and may vary considerably in volume, radioactivity, and chemical composition. A wide range of treatment methods have been used throughout the industry to treat these wastes. Treatment methods for LRWs have tended to use the same conventional processes found in industrial and municipal water treatment. These processes typically include chemical treatment, adsorption, filtration, ion exchange, and evaporation. They are limited by either their inability to remove all contaminants or, in evaporation, the high operating costs involved and the large quantities of secondary solid waste produced, which means that satisfactory processing of LRWs is difficult to achieve. Furthermore, the treated liquid effluent is not pure enough for environmental discharge or recycling. During the past 5-10 years, membrane technology has been gradually introduced into nuclear power plants for treatment of low radioactive waste.

An application of membrane methods for liquid radioactive wastes treatment requires solving many problems connected with the proper selection of the membranes, membrane modules and other equipment according to local conditions: chemical and radiochemical composition of the effluents treated, their activity and total salinity.

Membrane processes enable radioactive impurities to be separated from waste stream by selective passage of certain components of the stream through a membrane. These processes include reverse osmosis (RO), ultrafiltration (UF) or micro filtration (MF), depending on the pore size in the membrane. Membrane processes were already applied for radioactive laundry wastes in nuclear power plants, of mixed laboratory wastes, and for cleanup of boric acid solutions for recycling. There are many installations based on membrane technology, working successfully in nuclear industry.

The application of membrane processes limited to only low and probably medium level liquid wastes where the concentration of radioactivity limits to $37\text{-}3.7\times10^6$ Bq/L. The volume of waste is normally reduced by a factor of 10 and decontamination factor of 8-10 is achieved in this process (Pabby et al., 2009).

Various membrane-based methods have been developed for this purpose. The most important ones are reverse osmosis, nanofiltration, ultrafiltration, precipitation ultrafiltration, complexation ultrafiltration, microfiltration, osmotic concentrator, electrodialysis, electrodeionization, diffusion dialysis and Donnan dialysis, and liquid membranes. Only few methods have been commercialized until now. Table 1 shows some industrial use of membrane technology for nuclear liquid waste treatment.

Recently, a new process named membrane distillation (MD) has been introduced for this purpose. Membrane distillation is a separation method that employs porous liophobic membrane, non-wettable by the liquid. Because of liophobicity of the polymer, only vapor is transported through membrane pores. The condensation takes place on the other side of the membrane in air gap, cooling liquid or inert carrier gas. Usually MD is employed to treat water solutions, therefore hydrophobic membranes manufactured from polymers such as polypropylene (PP), polytetrafluoroehtylene (PTFE), or poly(vinylidenefluoride) (PVDF) are used in the process. The driving force in the MD process is a gradient of partial pressures of the components of the solution in gaseous phase. Despite of some technical and process limitations, membrane techniques are very useful methods for the treatment of different types of effluents. Removal of tritium from nuclear waste (liquid and gaseous effluents), isotope separation, gaseous radioactive wastes and noble gases separation are the latest applications of membrane technology in the field of radioactive materials processing industries (Zakrzewska-Trznadel et al., 2001) .

3.3. Air Pollution

Air pollution is most often affected by the emission of pollution generated by industry, power plants, car transport, and agricultural and municipal waste. Pollution is exceptionally hazardous when it involves the emission of so-called acid gases (SO_2, NO_X) and volatile organic compounds, mainly halogen-derived hydrocarbons and aromatic compounds which destroy the ozone layer and contribute to the creation of the greenhouse effect. Different methods are used to eliminate these substances. Particular techniques have been classified according to optimum range of concentration at which they are working. Appropriate combining of these processes (hybrid processes) can be advantageous from the economic and technical viewpoints. The removal of volatile organic compounds can be carried out

with the recovery of solvent or without it, although from environmental and economical viewpoints, the second solution is favored (Bodzek, 2000).

Membrane process	Facility	Wastes processed
Reverse osmosis	AECL Chalk River (Canada)	Reactor coolant clean-up with boric acid recovery
RO with conventional pretreatment	Nine Mile Point NPP (USA)	BWR floor drains and various other wastes
	Pilgrim NPP (USA)	
RO with ultrafiltration pretreatment	Wolf Creek NPP (USA)	PWR floor drains, reactor outage waste, spent resin sluice water, and other waste
	Comanche Peak NPP (USA)	Floor drains, resin sluice water, boron recycle water
	Dresden NPP (USA)	Inventory of TRU (trans-uranium) contaminated batch of liquid waste
	Bruce NPP (Canada)	Aqueous wastes from steam generator chemical cleaning
RO with microfiltration pretreatment	AECL Chalk River (Canada)	Nuclear research wastes
Ultrafiltration	Diablo Canyon NPP (USA)	Spent media transfer liquid
	River Bend NPP (USA)	BWR floor drains
	Salem NPP (USA)	PWR floor drains, equipment drains, and other various sources
	Seabrook NPP (USA)	PWR floor drains and spent resin tank drain-down
	Callaway NPP (USA)	Floor drains, equipment drains, reactor coolant
	Mound Laboratory (USA)	Wastes from fuel reprocessing activities
	Sellafield Nuclear Center (UK)	Alpha-containing tail wastes
	Projected facility for treatment of laundry (detergent) wastes	Laundry (detergent) wastes
Microfiltration	AECL Chalk River (Canada)	Contaminated ground water
	Rocky Flats (USA)	

Table 1. Examples of industrial use of membrane technology for nuclear waste processing (Pabby, 2008).

Another problem connected with pollution of the atmosphere is the generation of vast volumes of gases, which contributes to the creation of the greenhouse effect - carbon dioxide while burning carbon-derived fuels and simultaneous emission of methane and carbon dioxide from solid waste dumps. With respect to the latter case, it seems to be beneficial to recover methane since it is a valuable source of energy and is characterized by higher global greenhouse factor than carbon dioxide (Table 2).

Compound	Comparative index inducing greenhouse effect	Concentration*
CO_2	1	56
CH_4	32	25
Halogen derived hydrocarbons	ca. 15000	8
O_3	2000	9
NO	150	2

* relative concentration without taking nitrogen and oxygen into consideration.
Table 2. Influence of particular gases on the greenhouse effect (Bodzek, 2000).

The concept of gas separation through membranes is based on the mechanism of dissolution and diffusion. As compared to liquids, gases are characterized by low affinity to polymers and therefore their solubility in such materials is also low (usually <0.2%). Solubility of a given gas in polymer increases along with the increase in affinity to polymer; for example, the solubility of carbon dioxide is higher in hydrophilic polymers than in hydrophobic ones. Separation of gases and vapors has been applied practically in the industry for splitting the following systems (Li et al., 2008):
− CO_2/CH_4 - biogas, natural gas,
− H_2 or He from other gases,
− H_2S/CH_4 - natural gas,
− O_2/N_2 - oxygen enrichment of air and vice versa,
− H_2O - drying of gases,
− SO_2 - desulphurization of gases,
−   vapors of organic compounds - removal from the air and from industrial waste flows.

3.3.1 Removal of Volatile Organic Compounds from Air

Industrial processes where volatile organic solvents are applied contribute to the generation of waste gas flows polluted by the vapors of these compounds. They are not only hazardous for the environment but also have some kind of economic value connected with the recovery of chemical substances and energy. Selective membrane absorption used for the removal of volatile organic compounds integrates the advantages of absorption and membrane gas separation. The properties of such solutions are as below:
−   Compact capillary membranes are characterized by short diffusion path,
−   The surface of phase separation is taken up by the membrane,
−   The recovery of volatile organic compounds is taking place even at low concentrations,
−   Energy consumption is low,
−   The technique is not destructive,
−   Flexibility of process system.
A spin-off of the activities of gasoline vapor recovery at gasoline tank farms is the development of a system to reduce emissions generated by the operation of petrol stations. In the case of car refueling, the connection between the dispenser nozzles and the petroleum tank filler pipe is the only area open to the atmosphere. To reduce emissions during refueling, vacuum assisted vapor return systems have been introduced in many countries. An investigation of the TÜV Rheinland has shown that the efficiency of catching emissions by means of the 1:1 vapor return ratio is limited to an average of approx. 75%. The difference between a minimum value of 50% and a maximum value of 90% in vapor return

is caused by differences in the construction of car filling pipes. In order to enhance the vapor return rates, a surplus of air/vapor volume has to be returned. Tests have shown that the increase of the air over liquid ratio to 1.5:1 leads to an improvement of the efficiency of between 95–99%, depending on the type of the car. The enhancement of the vapor return rate is only possible if no additional emissions are generated. A membrane-based vapor separation system to treat the breather pipe vent gases of storage tanks enables emission reduction during car refueling without creating any additional emissions. The essential requirement is a leakage proof installation of tanks, pipes and dispensers. Furthermore, the installation of over/under pressure safety valves at breather pipes and check valves at the filling and vapor-balancing couplings of the storage tanks. Because of the surplus of returned vapor volume, a pressure build-up occurs in the storage tanks. At a given set point of a pressure gauge, which measures the differential pressure between tank pressure and atmospheric pressure, the vacuum pump of a membrane separation system is activated. This system is installed parallel to the vent stack of the storage tanks. A pneumatic valve in the retentate line of the membrane module is opened by the applied vacuum. The overpressure of the storage tanks causes a volume flow, which is released by passing the membrane stack. The gasoline vapors are separated from the off-gas and clean air enters to the atmosphere. After the lower set point of the pressure gauge, is reached, the system is deactivated. Besides the advantage of emission reduction, the wet stock losses of gasoline storage can be reduced because diffusive emissions are avoided and most of the generated gasoline vapor is returned to the storage tank. Because of the simplicity and the nearly maintenance free operation, the system is particularly suitable for petrol station applications and product delivering-receiving stations at petrochemical plants (Takht Ravanchi et al., 2009a).

3.3.2 Removal of SO$_2$ from Exhaust Gases

Various absorption processes are used for the removal of SO$_2$ from exhaust gases. One of the most commonly used is the so called "double alkaline process" which can also be applied to membrane absorbers. Pilot tests for an installation of the output of 100m^3/h by TNO (Holland) using the gas coming from the installation for biogas combustion, which contained SO$_2$. Sulfur dioxide, which was being recovered by membrane absorption in the form of sodium sulfite, may be again used in the production process. Over the 6 months of testing, over 95% of SO$_2$ was recovered with the output of 120m^3/h. There were no disturbances observed in the operation caused by fluctuations in the volume of gas flux or content of SO$_2$. Also, the fouling of membrane was not observed since in the process of gas separation only the diffusive transport of substances takes place, and convection transport (which is principally responsible for this process) is not observed (Bodzek, 2000).

3.3.3 Removal of CO$_2$ from Exhaust Gases

Conventional techniques for the removal of carbon dioxide from the air are based principally on the process of chemical and/or physical absorption. It is absorbed by solvents in low temperature and/or under low pressure. The following solvents are the most typical: monoethanoloamine (MEA), diethanoloamine (DEA), triethanoloamine (TEA), potassium carbonate (Benfield), methylodiethanoloamine (MDEA), methanol (Rectisol), N-methylo-2-

pyrolidon (Purisol), polyethylene glycol (Selexol), propylene carbonate (Fluor solvent) and the system sulfolane/diisopropanoloamine/water (Sulfinol).

Chemical solvents are used when the concentration of carbon dioxide in the air is low and when carbon dioxide obtained in the product should have high purity. But with the high concentration of carbon dioxide in the inlet gas and with smaller requirements involving its purity in the product, physical solvents are favored. Due to low partial pressure of carbon dioxide in exhaust gases, in practice the absorption/desorption process is applied with the use of monoethanoloamine. Absorption is carried out in the temperature only slightly higher than ambient temperature and desorption in the temperature of about $110^{o}C$. The required membrane surface in the absorption stage can be calculated from respective equations. Assuming that the transport index of matter is limited solely by the diffusion stage in gas filling membrane pores, we can accept that it equals to 0.02m/s for typical capillary membranes (l mm of external diameter). For the flow of exhaust gases at the rate of $600m^3/s$ and carbon dioxide recovery at the level 70%, the required membrane surface will be $35,500m^2$. Introductory economic analyses indicate that the cost of the absorber alone could be reduced by 30% and the total cost of the installation absorption/desorption can be reduced by 10%.

Recently, supported liquid membranes have been considered to be an effective means for removal of acidic components such as CO_2 and H_2S from natural gas and other process gases. In this process a thin layer of the absorption solvent placed in the pores of the membrane by capillary force. This very thin layer (approximately less than 150 µm) has negligible mass transfer resistance and with the high contact surface area between the phases due to the presence of membrane, mass transfer occurs as fast as possible. Heydari Gorji et al. used a supported liquid membrane containing amine solution as the carrier for gas sweetening. The experimental results from CO_2/H_2 separation showed the separation factor of 1350 and permeability of 95×10^{-11}(mol.cm/cm².s.kPa) at the ambient temperature and a transmembrane pressure of less than 2 barg is attainable (Heydari Gorji et al., 2009 a,b).

3.3.4 Purification of Air from Cigarette Smoke in Closed Rooms

Cigarette smoke contains a few hundred chemical compounds, in both the solid and gas phases. The existing systems of mechanical ventilation in houses and in offices do not guarantee good air quality with many heavy smokers around. The quality of the air indoors could be improved by the application of a portable facility for air purification, which enforces air circulation through a system of filters. Classical facilities for air purification make use of electrostatic or cloth filters and sometimes of filters from wood coal. However, most filters are not effective with respect to most gas substances generated during cigarette smoking. The problem can be solved by membrane filters. Experimental results showed even when tap water was used as the absorber (which has very low tendency for absorption of hydrocarbons) the efficiencies was very good. Compounds soluble in water were characterized by high removal effectiveness. The tests have proven that the tested membrane facilities for air purification are useful filtration systems which are characterized by high removal effectiveness of compounds soluble in water and small values of pressure drop. The facilities are compact due to the application of capillary modules. Table 3 shows the effectiveness of the membrane facility for purification of air containing cigarette smoke (Bodzek, 2000)

Component	Removal effectiveness [%]
Acetone	96.6
Styrene	15
Formaldehyde	98.4
Nicotine	99.1
Ammonia	95
Aroma	49-54

Table 3. Effectiveness of membrane facility for purification of air containing cigarette smoke (Bodzek, 2000).

4. Membranes for Process Intensification

4.1 Nano-composite Gas Separation Membranes

Membrane gas separations are attractive because of their simplicity and low energy costs, but often limited by insufficient gas flux. This problem is specially challenging because the permeability of a material is frequently inversely related to its selectivity. Recently, polymer–inorganic nano composite materials have been developed to improve the physical properties of polymer membranes. The polymer-inorganic nano composite membrane constitutes of two matrices, i.e. polymer and inorganic material. In these kinds of membranes, the inorganic phase is dispersed at nanoscale level in the polymer phase. Due to special structural characteristics of polymer-inorganic nano composites, the gas separation properties of pure polymers are improved.

Kong et al. used polyimide (PI)/TiO_2 nano composite membranes for gas separation. The permeation properties of these membranes are illustrated in Table 4. As it can be seen from these results, the low TiO_2 content could not greatly enhance the permeation properties of the composite membranes. When the TiO_2 content in the composite membranes was above 20 wt%, the permeability of the composite membranes was remarkably enhanced, and selectivity of the composite membranes was still kept at a high level. This might be caused by the specific interaction between gases and the TiO_2 component in PI/TiO_2 composite membranes. At TiO_2 content of 25wt%, the results were very interesting because both of the permeability and selectivity of PI membrane were enhanced at the same time (Kong et al. 2002).

Zhang et al. used nano-sized nickel-filled carbon membranes to examine gas separation properties. Nickel, as a very commonly used hydrogenation catalyst was chosen because it can selectively chemically adsorb hydrogen, which would result in the change of hydrogen permeation properties of the resulting nickel-filled carbon membranes. Permeation properties of single gas through Ni-filled carbon membranes are shown in Table 5. It could be seen that the nickel amount had strong influence on the gas permeation properties of the corresponding membrane (Zhang et al., 2006).

TiO_2 content (wt%)	P_{H2}	P_{O2}	P_{N2}	P_{CH4}	$\alpha_{H2/N2}$	$\alpha_{H4/CH4}$	$\alpha_{O2/N2}$
0	3.809	0.166	0.023	0.018	166.9	214.0	9.3
5	3.773	0.155	0.033	0.018	115.0	222.0	4.7
15	5.523	0.273	0.053	0.039	104.6	142.2	5.2
20	6.686	0.290	0.037	0.041	180.7	163.4	7.8
25	14.143	0.718	0.075	0.099	187.5	143.2	9.5

Table 4. Permeability (barrer) and selectivity of PI/TiO_2 composite membrane with different TiO_2 content (Kong et al. 2002).

Ni content (wt%)	P_{H2}	P_{CO2}	P_{O2}	P_{N2}	$\alpha_{H2/N2}$	$\alpha_{CO2/N2}$	$\alpha_{O2/N2}$	$\alpha_{CO2/H2}$
1	5.6	21	3.6	0.3	19	70	12	3.7
3	1.8	31	6.1	0.6	3.0	52	10	17
5	0.8	30	8.5	6.8	0.1	4.4	1.3	38
7.5	3.0	29	10.2	7.2	0.4	4.0	1.4	9.7
10	10	22	4.5	4.3	2.3	5.1	1.0	2.2

Table 5. Single gas permeance (10^{-10} mol m^{-2} s^{-1} Pa^{-1}) and ideal selectivity of Ni-filled carbon membranes with different amounts of nano-sized nickel (Zhang et al., 2006)

4.2 Olefin-Paraffin Separation via Facilitated Transport Membrane

Olefins such as ethylene and propylene are important feedstocks in petrochemical industry. They are used for the production of polypropylene, acrylonitrile, propylene oxide, oxo alcohols, cumene, acrylic acid and isopropyl alcohol. As olefin and its corresponding paraffin are produced simultaneously in the petrochemical complexes, the important step is their separation (Takht Ravanchi et al., 2008a-d).

The traditional and most conventional separation method is cryogenic distillation. As olefin and its corresponding paraffin have close physical properties and relative volatility of this separation is near unity (α~1.2), distillation is hard. A very tall column containing around 200 trays that operated at high pressure (20bar) and low temperature (-30°C) is required for this separation. Because of the high fixed and operating costs of such a column, proposing an alternative process that can be performed at moderate operating condition is the aim of researchers in recent years.

Since membrane processes have many advantages; such as simplicity, energy-saving, easy operation, environment friendly, low-maintenance cost and modular configuration; in recent years researchers investigated their application for olefin-paraffin separation. At first polymeric membranes were used for this separation. Burns & Koros, 2003 reported separation factors obtained for the separation of 50:50 (vol. %) propylene-propane mixture using polymeric membranes. The highest separation factor obtained was 21 (when Pyralin 2566 was used as membrane (Krol et al., 2001)), which is so low for industrial applications.

Facilitated transport (FT) phenomena helped impressively in the utilization of membrane for olefin-paraffin separation. Park et al., 2001 and Kim et al., 2003 reported the application of solid polymer electrolyte (SPE) membranes, one type of FT membranes, for propylene-propane separation. In comparison with polymeric membranes higher separation factors were obtained (170 in PAAm/AgBF$_4$ membrane containing 67mol.% Ag$^+$ (Park et al., 2001)).

In SPE membranes, monomer and carrier ion (Ag$^+$) were incorporated in the membrane in the procedure of membrane preparation. In immobilized liquid membranes (ILMs), as another type of FT membranes, the porous support was immersed in the carrier solution. Carrier ions were settled inside the pores by capillary forces.

Immobilized liquid membranes were not studied for propylene-propane separation before. As their preparation is somehow easier than SPE membranes, their application for propylene-propane separation seems more feasible.

In a membrane separation setup which contains flat sheet membrane module, propylene-propane separation was studied. The detail description of the setup can be found in Takht Ravanchi et al., 2009b. Industrial grade propylene (99.74 mol.%) and industrial grade propane (99.79 mol.%) were used as feed gases. PVDF flat sheet membrane was used as the

support of ILM and AgNO₃ solution was used as carrier. Separation experiments were conducted at four trans-membrane pressures, four carrier concentrations and with three feed mixtures (Figure 2). As it can be seen, increasing trans-membrane pressure and carrier concentration are in favor of propylene separation. The results obtained confirm that present ILM system performs better in comparison with SPE membranes used for propylene-propane separation. For industrial application of this system, some pilot experiments must be conducted by which optimum values of operating conditions can be determined (Takht Ravanchi et al., 2009c-f).
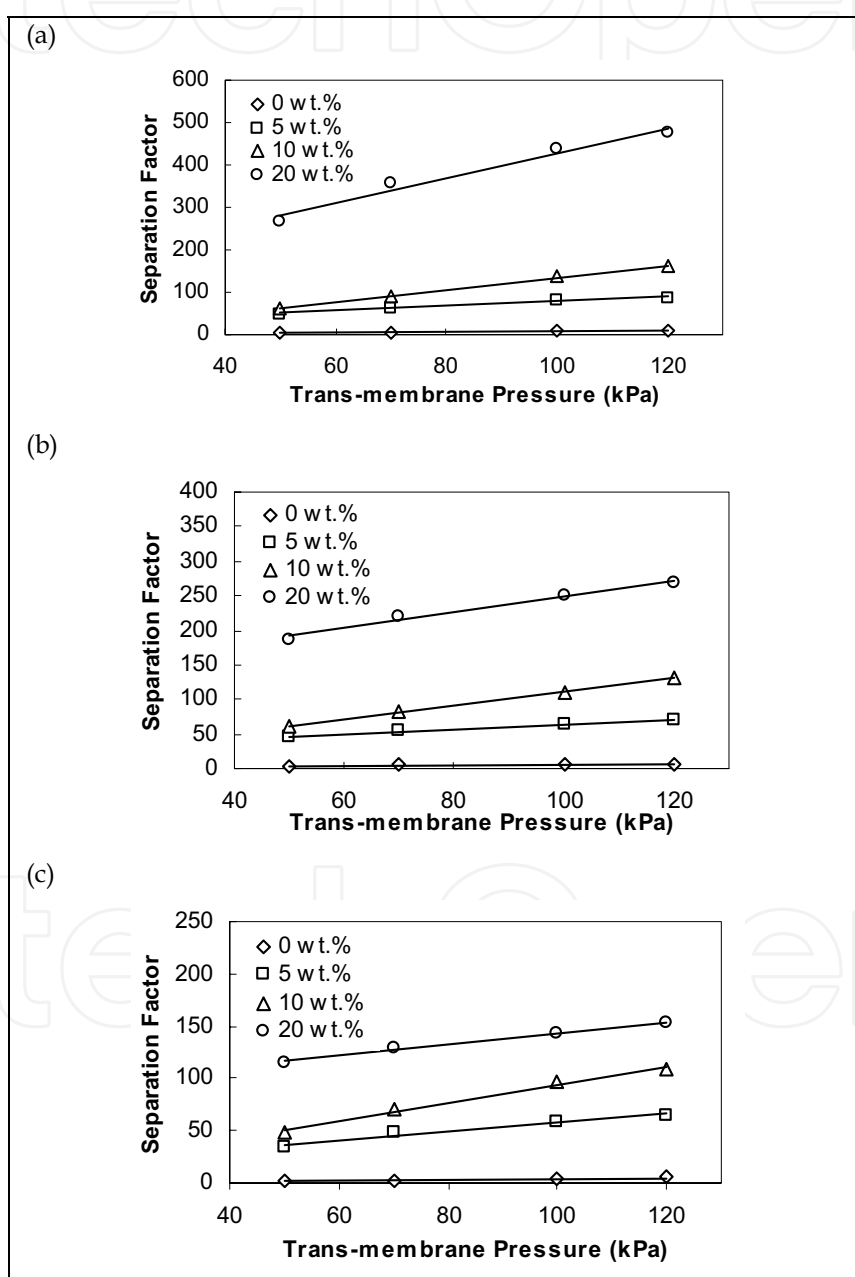
Fig. 2. Separation performance of PVDF-AgNO₃ ILM system for propylene-propane separation; (a) 30:70 (vol.%) propylene-propane mixture, (b) 50:50 (vol.%) propylene-propane mixture, (c) 70:30 (vol.%) propylene-propane mixture (Takht Ravanchi et al., 2008b)

4.3 Separation of Light Hydrocarbons

Pervaporation offers the possibility of separating solutions, mixtures of components with close boiling points, or azeotropes that are difficult to separate by distillation or other means. The first systematic work on pervaporation was done at American Oil in the 1950s. The process was not commercialized at that time and remained a mild academic curiosity until 1982, when GFT (Gesellschaft für Trenntechnik GmbH, Germany) installed the first commercial pervaporation plant. That plant separated water from concentrated alcohol solutions; GFT has since installed more than 50 such plants. In these plants, polyvinyl alcohol is used as composite membranes; they are far more permeable to water than alcohol. A flow scheme of a GFT plant combining distillation and pervaporation to produce dry alcohol is shown in Figure 3. The ethanol feed to the membrane generally contains ~10% water. The pervaporation process removes the water as the permeate, producing pure ethanol with less than 1% water and avoiding all the problems of azeotropic distillation.
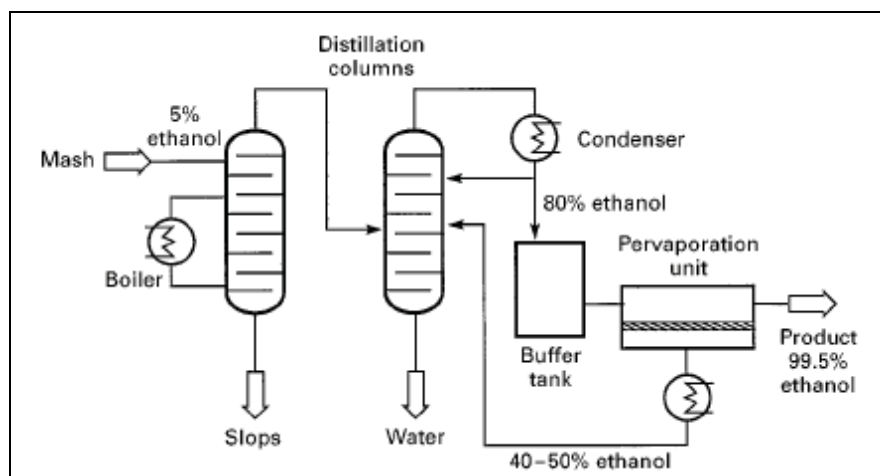

Fig. 3. Flow scheme of a GFT plant for ethanol recovery (Baker, 2000)

Spurred on by this success, a great deal of effort is being made to apply pervaporation to other difficult separations. Another commercial pervaporation application is the separation of dissolved VOCs (Volatile Organic Compound) from water, developed by Membrane Technology and Research, Inc. Relatively hydrophobic composite membranes, such as silicone rubber coated on a microporous polyimide support membrane, are used. Extremely high separation factors can be obtained for the more hydrophobic VOCs such as toluene, benzene, chlorinated solvents, esters and ethers.

Another commercial pervaporation processes involve the separation of organics and water. This separation is relatively easy, because organic solvents and water have very different polarity and exhibit distinct membrane permeation properties. The first pilot-plant result for an organic-organic application, the separation of methanol from methyl t-butyl ether/isobutene mixtures, was reported by Separex in 1988. This is a particularly favorable application and available cellulose acetate membranes achieve a good separation. More recently, Exxon started a pervaporation pilot plant for the separation of aromatic/aliphatic mixtures, using polyimide/poly urethane block copolymer membranes. This separation is one of the major separation problems in refineries (Baker, 2000).

4.4 Solvent Dewaxing

A promising new application of reverse osmosis in the chemical industry is the separation of organic/organic mixtures. These separations are difficult because of the high osmotic pressures that must be overcome and because they require membranes that are sufficiently solvent resistant to be mechanically stable, but are also sufficiently permeable for good fluxes to be obtained.

One application that has already reached the commercial stage is the separation of small solvent molecules from larger hydrocarbons in mixtures resulting from the extraction of vacuum residual oil in refineries. Figure 4a shows a simplified flow diagram of a refining lube oil separation process- these operations are very large. In a typical 100,000 barrel/day refinery about 15,000barrel/day of the oil entering the refinery remain as residual oil. A large fraction of this oil is sent to the lube oil plant, where the heavy oil is mixed with 3 to 10 volumes of a solvent such as methyl ethyl ketone and toluene. On cooling the mixture, the heavy wax components precipitate out and are removed by a drum filter. The light solvent is then stripped from the lube oil by vacuum distillation and recycled through the process. The vacuum distillation step is very energy intensive because of the high solvent-to-oil ratios employed. In 1998, a reverse osmosis process developed by Mobil for this separation is illustrated in Figure 4b. Polyimide membranes formed into spiral-wound modules are used to separate up to 80% of the solvent from the dewaxed oil. The membranes have a flux of 10-20gal/ft²day at a pressure of 450-650psi. The solvent filtrate bypasses the distillation step and is recycled directly to the incoming oil feed. The net result is a significant reduction in the refrigeration load required to cool the oil and in the size and energy consumption of the solvent recovery vacuum distillation section (Baker, 2001).

Mobil is now licensing this technology to other refineries. Development of similar applications in other operations is likely. Initially, applications will probably involve relatively easy separations such as the separation of methyl ethyl ketone/toluene from lube oil described above or soybean oil from hexane in food oil production. Long term, however, the technology may become sufficiently advanced to be used in more important refining operations, such as fractionation of linear from branched paraffins, or the separation of benzene and other aromatics from paraffins and olefins in the gasoline pool.
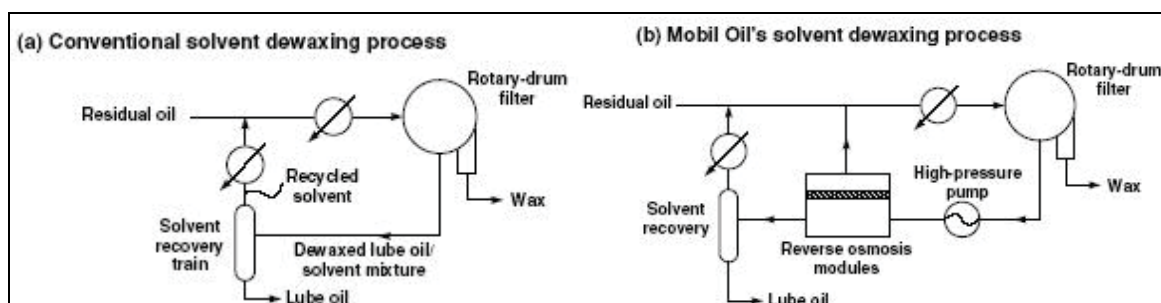

Fig. 4. Simplified flow schemes of (a) a conventional and (b) Mobil Oil's membrane solvent dewaxing processes (Baker, 2001)

4.5 Membrane Aromatic Recovery System

Phenolic compounds are used in phenolic resins, polycarbonates, biocides and agrochemicals. Aromatic amines are used in a wide range of consumer products, including polyurethane foam, dyes, rubber chemicals and pharmaceuticals. The factories that

manufacture and/or use these types of chemicals often create aqueous waste streams containing significant (0.1-10 wt%) amounts of aromatic amines or phenolic compounds. Phenol is an aromatic acid, with a solubility of 8 wt.% in water at 25°C. This compound is highly toxic and one of the EPA's priority pollutants. Two of the main commercial applications for phenol are production of bisphenol A and phenol-formaldehyde resins. Phenol and formaldehyde are the main reagents in the phenol-formaldehyde resin production process. Since phenol is highly toxic and at high concentration (>200mg/l) are inhibitory to biological treatment, the recovery of phenol from industrial wastewater streams has generated significant interest. Methods for the recovery of phenol include solvent extraction, activated carbon and polymer adsorption, and membrane processes.

Membrane technologies have attracted attention for removal of low-volatility organics from wastewaters. Porous membranes have been used for membrane solvent extraction for the recovery of organics from aqueous solutions. However, porous membranes have a major shortcoming due to their instability, i.e. breakthrough of the immobilized phase in the pores can occur unless a high breakthrough pressure through the membrane is maintained. Nonporous membranes were proposed for carrying out extraction. Compared to porous membranes, the breakthrough pressure is much higher through nonporous membranes; however, this is at the expense of a lower mass transfer rate in the membrane extraction.

The Membrane Aromatic Recovery System (MARS) is a relatively new process for recovery of aromatic acids and bases. In the MARS process aromatics are selectively removed from a wastewater stream into the stripping solution via a tubular silicone rubber membrane with a wall thickness of 500 µm. For aromatic bases (e.g. aniline) the stripping solution is maintained at an acidic pH using HCl and for aromatic acids (e.g. phenol) the stripping solution is maintained at a basic pH using NaOH (Ferreira et al., 2005).

The mass transfer rate of water through the membrane is negligible due to the hydrophobicity of the tubular silicone rubber membrane, combined with its relatively large thickness. Ion transport is also negligible; hence the ionic form of the aromatic, formed in the stripping solution, cannot pass back across the membrane into the wastewater solution. This not only keeps the aromatic in the stripping solution but also maintains the driving force across the membrane. MARS technology has been successfully applied for the recovery of phenol and aniline at lab and pilot plant scale. It has also been applied on full plant scale for recovery of p-cresol since December 2002 at a Degussa plant in Knottingley UK (Daisley et al., 2006).

4.6 Membrane Bio-Reactor

Activated sludge processes (ASPs) have widely been used for biological wastewater and sewage treatment. However, since the settling of activated sludge for solid-liquid separation is difficult by gravitational settling, the biomass concentration which can be controlled is limited to approximately 5000mg/L. Therefore, bio-reactor volume becomes large. On account of the difficulty of solid-liquid separation in biological wastewater treatment, a MBR has been one of the most prevalent solutions since late 1960s.

Membrane bio-reactor technology combines the biological degradation process by activated sludge with a direct solid-liquid separation by membrane filtration. By using micro or ultra filtration membrane technology (with pore sizes ranging from 0.05 to 0.4 µm), MBR systems allow the complete physical retention of bacterial flocs and virtually all suspended solids within the bioreactor. As a result, the MBR has many advantages over conventional

wastewater treatment processes. These include small footprint and reactor requirements, high effluent quality, good disinfection and odor control capability, higher volumetric loading and less sludge production (Wisniewski, 2007).

As a result, the MBR process has now become an attractive option for the treatment and reuse of industrial, domestic and municipal wastewaters, as evidenced by their constantly rising numbers and capacity. There are more than 2200 MBR installations in operation or under construction worldwide. In North America, 258 full-scale MBR plants have been constructed, where 39 of them are for industrial waste water treatment and 7 of them have been constructed for industrial chemical wastewater treatment. The current MBR market has been estimated to value around US$216 million and to rise to US$363 million by 2010 (Atkinson, 2006). Wastewater in petrochemical industry is currently treated by activated sludge process with pretreatment of oil/water separation. Tightening effluent regulations and increasing need for reuse of treated water have generated interest in the treatment of petrochemical wastewater with the advanced MBR process.

Tam et al. used a membrane bio-reactor/reverse osmosis (MBR/RO) and microfiltration-reverse osmosis (MF/RO) system for reclamation and reuse of wastewater. A schematic of these two systems is given in Figure 5. As it can be seen, in MBR/RO operation, there is no need to use "primary treatment" and "secondary treatment" and this is an advantage of MBR/RO system. The performance of these two systems is represented in Table 6 (Tam et al., 2007).

Parameter	MBR/RO system			MF/RO system		
	Feed	MBR effluent	RO permeate	Feed	MBR effluent	RO permeate
BOD_5 (mg/L)	198	<2	<2	3	<2	<2
CODcr (mg/L)	391	17.5	<2	23	17.9	<2
SS (mg/L)	201	<2	<2	2	<2	<2
E. coli (cell/L)	$4.1*10^7$	3.4 (44.3%)	ND	$2.8*10^7$	2 (19.7%)	ND
TKN (mg/L)	43.0	1.6	0.1	3.1	1.5	0.4

E. coli: Escherichia coli   SS: Suspended Solid
ND: Not Detected   TKN: Total Kjeldahl Nitrogen (the sum of organic N_2, NH_3 and $NH4^+$)

Table 6. Performance of MBR/RO and MF/RO systems (Tam et al., 2007)

5. Conclusion

Increasing research of membrane technology indicates that membranes definitely will become another alternative for industrial processes. However, much research and development effort is needed in order to commercialize membranes in the international market. The increased world-wide competitiveness in production has forced industry to improve current process designs and also the increased importance of natural environment has compelled industry to develop new process designs. Consequently, the development of new process designs using alternative technologies is of growing importance to the industry. A continuous research work on membrane properties and fundamental aspects of transport phenomena in the various membrane operations is important for the future of

membrane science and technology. There is a need for both basic and applied research to develop new membranes with improved properties and new membrane processes.
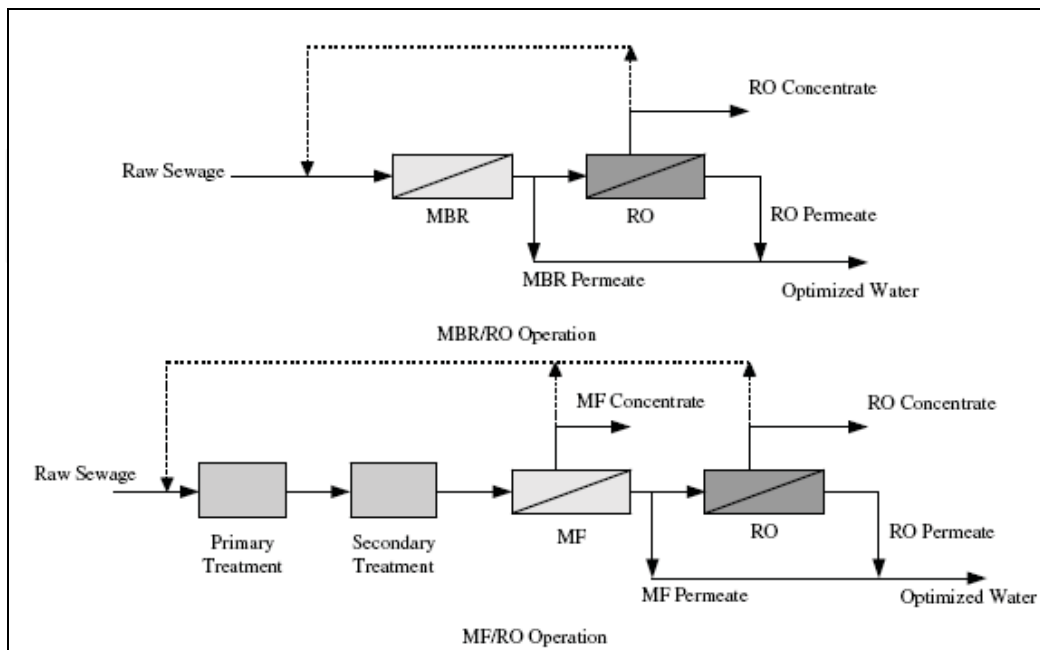

Fig. 5. An illustration of MBR/RO and MF/RO systems (Tam et al., 2007)

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Advanced Technologies

Edited by Kankesu Jayanthakumaran

This book, edited by the Intech committee, combines several hotly debated topics in science, engineering, medicine, information technology, environment, economics and management, and provides a scholarly contribution to its further development. In view of the topical importance of, and the great emphasis placed by the emerging needs of the changing world, it was decided to have this special book publication comprise thirty six chapters which focus on multi-disciplinary and inter-disciplinary topics. The inter-disciplinary works were limited in their capacity so a more coherent and constructive alternative was needed. Our expectation is that this book will help fill this gap because it has crossed the disciplinary divide to incorporate contributions from scientists and other specialists. The Intech committee hopes that its book chapters, journal articles, and other activities will help increase knowledge across disciplines and around the world. To that end the committee invites readers to contribute ideas on how best this objective could be accomplished.

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