

# Application of membrane separation processes in petrochemical industry: a review

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## Abstract

In this paper a general review on different membrane processes and membrane reactors was done. As the main aim of this paper is to review the application of membrane processes in petrochemical industry, processes such as olefin/paraffin separation, light solvent separation, solvent dewaxing, phenol and aromatic recovery, dehydrogenation, oxidative coupling of methane and steam reforming of methane were discussed in detail. Besides, separation using polymer-inorganic nano composite membranes and wastewater treatment using membrane bio-reactors were reviewed.

**Keywords:** Membrane process; Facilitated transport; Olefin; Paraffin; Nano composite membrane; Pervaporation; Reverse osmosis (RO); Membrane aromatic recovery system (MARS); Dehydrogenation; Oxidative coupling of methane (OCM); Steam reforming of methane (SMR); Water gas shift (WGS) reaction; Membrane bio-reactor (MBR)

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## 1. Introduction

Nowadays, membrane technologies are becoming more frequently used for separation of wide varying mixtures in the petrochemical-related industries and can compete successfully with traditional schemes [1–5]:

- The technology behind membrane gas separation is potentially an energy-saving one, because the separation process takes place without phase transition.
- It is also better for the environment, since the membrane approach requires the use of relatively simple and non-harmful materials.

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- The recovery of minor but valuable components from a main stream using membranes can be done without substantial additional energy costs.
- Compared with conventional techniques, membranes can offer a simple, easy-to-operate, low-maintenance process option.
- The development of novel materials for gas membrane manufacturing such as organic polymeric, hybrid organic-inorganic and inorganic will expand the use of membrane technology into new fields of applications in the petrochemical industry.
- The process is simple.
- There are diverse applications which can be studied by the same basic formulations.
- The process is generally carried out at atmospheric conditions which, besides being energy efficient, can be important for sensitive applications encountered in pharmaceutical and food industry.
- Modules can be added and optimized in a process design to achieve the desired separation.
- Their systems have a low capital cost, compact size, modular configuration, and low specific power consumption, which reduce the production cost.
- It is a clean process and requires simple and inexpensive filtration.
- The process is continuous and the membranes do not require regeneration, unlike the adsorption or the absorption processes, which require a regeneration step leading to the use of two solid beds or a solvent regeneration unit.

In the petrochemical industry, olefins such as ethylene and propylene are the most important chemicals used for the production of polyolefins such as polyethylene, polypropylene, styrene, ethyl benzene, ethylene dichloride, acrylonitrile, and isopropanol. An important step in the manufacture of olefins is large-scale separation of the olefin from the corresponding paraffin [6]. Furthermore, dehydrogenation, oxidative coupling of

methane, steam reforming of methane and water gas shift reaction are some important reactions in petrochemical industry.

Membrane gas separation is attractive because of its simplicity and low energy cost, but it has one major drawback and that is a reverse relationship between selectivity and permeability. Nano composite membranes, in which selectivity and permeability can simultaneously be improved, solve this problem.

Petrochemical waste streams may contain phenolic compounds or aromatic amines. They are highly toxic and at high concentrations are inhibitory to biological treatment. Membrane aromatic recovery system (MARS) is a relatively new process for recovery of aromatic acids and bases.

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 membrane bio-reactor (MBR) process.

In this paper, membrane and their application in some important petrochemical processes, nano composite membranes and membrane bioreactors are reviewed.

## **2. What is a membrane?**

Membrane is defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 10 microns to few hundred micrometers. The principal types of membrane are shown sche-

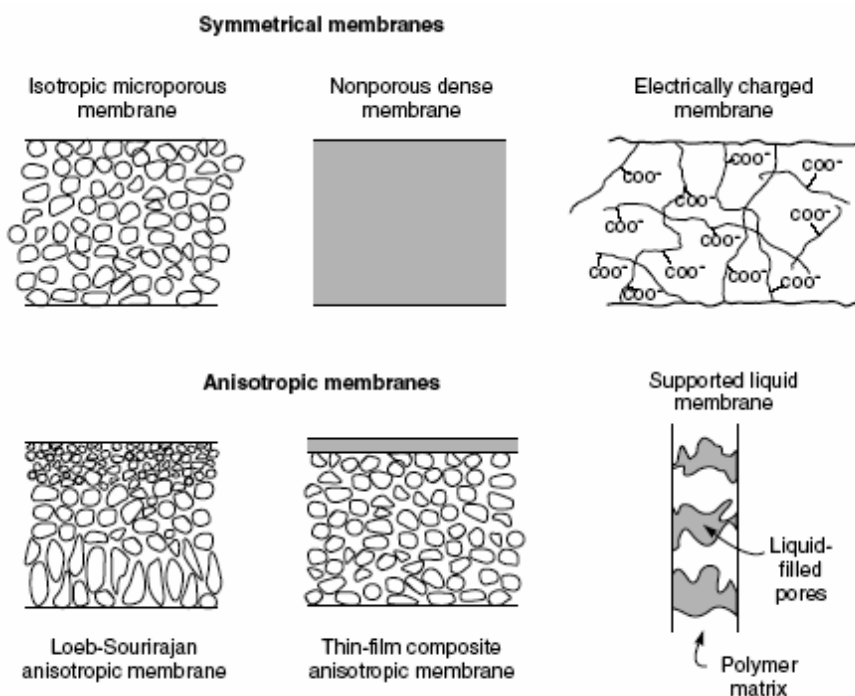


Fig. 1. Schematic diagrams of principal types of membranes [7].

matically in Fig. 1 and can be classified as below [7–10]:

- Isotropic membranes
  - Microporous membranes
  - Nonporous, dense membranes
  - Electrically charged membranes
- Anisotropic membranes
- Ceramic, metal and liquid membranes

### 3. Membrane processes

Transport through the membrane takes place when a driving force is applied to the components in the feed. In most of the membrane processes, the driving force is a pressure difference or a concentration (or activity) difference across the membrane. Parameters such as pressure, concentration (or activity) and even temperature may be included in one parameter, the chemical potential  $\mu$ .

Another driving force in membrane separations is the electrical potential difference. This driving force only influences the transport of charged particles or molecules. The membrane processes, according to their driving forces, are classified in Table 1 [11]; the status of developed, developing and yet-to-be developed industrial membrane technologies is summarized in Table 2 [7] and a detail explanation of different membrane processes is represented in Table 3.

#### 3.1. Gas separation by membranes

The separation of mixtures of gases is performed with the objective of obtaining one or more of the constituents in a pure form. There are many applications in both large scale and small scale processes. Separation can be achieved by several methods based on different physical and chemical properties of the species.

Table 1

Classification of membrane processes according to their driving forces [11]

Pressure difference	Concentration (activity) difference	Temperature difference	Electrical potential difference
Microfiltration	Gas separation	Membrane distillation	Electrodialysis
Ultrafiltration	Pervaporation		
Nanofiltration	Carrier mediated transport		
Reverse osmosis	Dialysis		
Piezodialysis	Diffusion dialysis		

Table 2

Status of membrane processes [7]

Category	Process	Status
Developed industrial membrane separation technologies	Microfiltration, ultrafiltration, reverse osmosis, electrodialysis	Well-established unit operations. No major breakthroughs seem imminent.
Developing industrial membrane separation technologies	Gas separation, pervaporation	A number of plants have been installed. Market size and number of applications served are expanding.
To-be-developed industrial membrane separation technologies	Carrier facilitated transport membranes, piezodialysis	Major problems remain to be solved before industrial systems will be installed on a large scale

There are four important methods applied to the separation of gases: absorption, adsorption, cryogenics and membranes (Table 4). Process economics will determine which of these methods is used for any particular applications [8,22–28].

Membrane separation based on “selective” gas permeation competes directly with other three mentioned methods in many applications. Membranes offer versatility and simplicity in comparison to other methods, which must be balanced against limitations of medium purity and the need for recompression [22]. All the membrane separation processes have the common feature that separation is achieved via a membrane.

This process competes with technology alternatives such as adsorption, cryogenic distillation, etc in niche application areas. The membrane process has certain advantageous, i.e. compactness and light in weight, low labor intensity, modular design permitting easy expansion or operation at

partial capacity, low maintenance (no moving parts), low energy requirements and low cost.

Membranes made of polymers and copolymers in the forms of flat film or hollow fibers have been used for gas separation. It is possible even with the two extreme types of membrane considered, i.e. porous and nonporous. The transport mechanisms through these two types of membrane are completely different. In porous membranes when gas transport takes place by viscous flow, no separation is achieved because the mean free path of the gas molecules is very small relative to the pore diameter. By decreasing the pore diameter of the pores in the membrane, the mean free path of the gas molecules may become greater than the pore diameter. This kind of gas flow is called Knudsen flow. The separation of two gases by a Knudsen flow mechanism depends on the ratio of the square root of their corresponding molecular weights. This means that low separation factors are gener-

Table 3  
A detail explanation of different membrane processes [11–21]

Pressure driven membrane processes					
	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis	Piezodialysis
Membrane	(A)symmetric porous	Asymmetric porous	Composite	Asymmetric or composite	Mosaic membranes
Thickness	≈ 10–150 μm	≈ 150 μm	Sublayer ≈ 150 μm Top layer <1 μm	Sublayer ≈ 150 μm Top layer <1 μm	≈ a few hundred μm
Pore size	≈ 0.05–10 μm	≈ 1–100 nm	≈ 2 nm	< 2 nm	Nonporous
Separation principle	Sieving mechanism	Sieving mechanism	sieving and electrostatic repulsion	Steric and electrostatic repulsion	Ion transport
Membrane material	Polymeric, ceramic	Polymer, ceramic	polyamide	cellulose triacetate, aromatic polyamide, polyamide and poly (ether urea)	Cation/anion- exchange membrane
Concentration driven membrane processes					
	Gas separation	Pervaporation	Carrier mediated transport	Dialysis	Diffusion dialysis
Membrane	Asymmetric or composite membranes with an elastomeric or glassy polymeric top layer	Composite membranes with an elastomeric or glassy polymeric top layer	Supported liquid membrane (SLM), emulsion liquid membrane (ELM), fixed carrier membranes, solvent swollen membrane	Homogenous	Ion exchange membranes
Thickness	≈ 0.1 to a few μm (for top layer)	≈ 0.1 to a few μm (for top layer)	20–150 μm (SLM), ≈ 0.1–1 μm (ELM)	10–100 μm	≈ a few hundred μm (100–500 μm)
Pore size	nonporous (or porous <1 μm)	nonporous	Nonporous		
Separation principle	Solution/diffusion (nonporous membrane) Knudsen flow (porous membrane)	solution/diffusion	Affinity to carrier (carrier mediated transport)	Difference in diffusion rate, solution/diffusion	Donnan exclusion mechanism
Membrane material	Elastomeric and glassy polymer	Elastomeric and glassy polymer	Hydrophobic porous membrane as a support	Hydrophilic polymers	Anion/cation exchange membrane

Table 3  
Continued

Thermally driven membrane processes	
Membrane distillation	
Membrane	Symmetric or asymmetric porous
Thickness	20–100 $\mu\text{m}$
Pore size	$\approx 0.2\text{--}1.0 \mu\text{m}$
Separation principle	Vapor-liquid equilibrium
Membrane material	Hydrophobic (polytetrafluoroethylene, polypropylene)
Electrically driven membrane processes	
Electrodialysis	
Membrane	Cation-exchange and anion-exchange membranes
Thickness	$\approx$ a few hundred $\mu\text{m}$ (100–500 $\mu\text{m}$ )
Pore size	Nonporous
Separation principle	Donnan exclusion mechanism
Membrane material	Hydrophobic (polytetrafluoroethylene, polypropylene)

Table 4  
A comparison between gas separation technologies [22]

Technology	Advantages	Disadvantages
Cryogenic (without distillation)	High recovery of products Moderate purity of light products (e.g. H <sub>2</sub> up to 98%) Can operate at high pressures Low cost Low pressure loss of light product	Cannot achieve very high purity of light products
Cryogenic (with distillation)	High recovery of products High purity of light products (e.g. H <sub>2</sub> up to 99.5%) when using hydrocarbon wash processes Can operate at high pressures Good purity of heavy products Low pressure loss of light product	High cost High energy consumption
Absorption	Simple process Low pressure loss of light product	Poor separation characteristics, i.e. low purity light ends or low recovery of heavy ends
Adsorption (pressure swing)	Very high purity of light product (e.g. 99.99% H <sub>2</sub> ) Simple process	Low recovery Operates most favorably at lower pressures (20–30 bar)
Adsorption (thermal swing)	Can remove minor components virtually completely	Expensive for bulk removal of impurities

ally obtained. High separation can only be achieved via a cascade operation involving a number of modules connected together [11]. Where the transport of gases occurs through nonporous membranes, Knudsen flow is not involved. However, when these nonporous membranes are used in a composite membrane where a dense top layer is supported by a porous substructure, Knudsen flow may contribute to the total flow depending on the pore sizes in the sub layer. Gas separation through nonporous membranes depends on differences in the permeabilities of various gases through a given membrane [11,29–31]. Ideal gas separation membranes possess a high flux and selectivity. However, generally a trade-off can be observed, i.e., high fluxes or high permeabilities are related to low selectivities and vice versa. High permeable materials are used if high selectivities are not required. If a moderate selectivity is required, then low permeable materials based on

glassy polymers will be employed. In practice, a balance must be found between permeability and selectivity.

The process of gas permeation is a relatively simple process which has expanded in use rapidly since it was introduced commercially in 1979. Since that time approximately 20 or more companies have come to the market place with equipment. The range of applications covers the supply of pure or enriched gases such as He, N<sub>2</sub> and O<sub>2</sub> from air, the separation of acid gases such as CO<sub>2</sub> and H<sub>2</sub>S, the separation of H<sub>2</sub> in the petrochemical and chemical industries and a variety of smaller applications [22]. Table 5 shows applications established in the field of membrane gas separation [32]. An overview of various applications and materials can be found in the literature [7,11,33–40].

Separation of olefin and paraffin gases is one of the most important processes in the petrochemi-

Table 5  
Gas membrane applications and suppliers [32]

Gas separation	Application	Suppliers
O <sub>2</sub> /N <sub>2</sub>	Nitrogen generation, oxygen enrichment	A/G Technology, Permea (Air Products), Generon (Messer), IMS (Praxair), Medal (DuPont, Air Liquide), Aquilo (Parker Hannifin), Ube
H <sub>2</sub> /hydrocarbons	Refinery hydrogen recovery	Air Products, Air Liquide, Praxair
H <sub>2</sub> /CO	Syngas ratio adjustment	Air Products, Air Liquide, Praxair
H <sub>2</sub> /N <sub>2</sub>	Ammonia purge gas	Air Products, Air Liquide, Praxair
CO <sub>2</sub> /hydrocarbon	Acid gas treating, enhanced oil recovery, landfill gas upgrading	Kvaerner (Grace Membrane System), Air Products, Ube
H <sub>2</sub> S/hydrocarbon	Sour gas treating	Kvaerner (Grace Membrane System), Air Products, Ube
H <sub>2</sub> O/hydrocarbon	Natural gas dehydration	Kvaerner, Air Products
H <sub>2</sub> O/air	Air dehydration	Air Products, Ube
Hydrocarbons/air	Pollution control, hydrocarbon recovery	MTR, GMT, NKK
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery	MTR, GMT, SIHI

cal industry. In 1998, the United States produced 52 billion pounds of ethylene and 29 billion pounds of propylene [41]. Various petrochemical streams contain olefin and other saturated hydrocarbons. These streams typically originate from steam cracking units (ethylene production), catalytic cracking units (motor gasoline production), or the dehydrogenation of paraffins [42–47]. During the years, different processes have been used for the separation of olefin-paraffin mixtures, such as low-temperature distillation, extractive distillation, physical or chemical adsorption and physical or chemical absorption [28].

Currently, this separation is carried out by cryogenic distillation, which is highly energy-intensive due to the cryogenic temperatures required for the process and low relative volatilities of components. Distillation columns are often up to 300 ft tall and typically contain over 200 trays. With reflux ratios greater than 10, a very high energy input is required for the distillation process. This large capital expense and energy cost have created incentive for extensive research in this area

of separations, and membrane separations have been considered as an attractive alternative [48–56]. In searching for membrane materials, one generally looks not only for a favorable combination of required permeability and selectivity, but also for an improvement in mechanical properties of the membrane [1].

### 3.1.1. Solid membranes

As olefin/paraffin separation is an important process in petrochemical industry, in this section the use of solid membranes in this process is reviewed. Furthermore, the application of nanotechnology in the production of membranes and their separation performance is investigated.

#### 3.1.1.1. Olefin/paraffin separation using solid membrane systems

Different researchers had used various polymeric membranes, in order to investigate the performance of propylene/propane separation sys-



Table 6  
C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> permeation data in polymeric membranes

Polymer <sup>1</sup>	Temperature (°C)	Feed pressure	Propylene permeability (Barrer <sup>2</sup> )	Selectivity C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>	Reference
Matrimid	26	2–3 bar	0.10	16	57
Matrimid-Thermid 85/15	26	2–3 bar	0.03	4	57
Pyralin 2566	26	2–3 bar	0.09	21	57
Torlon AI-10	26	2–3 bar	<0.02	—	57
PPO	30	2–4 bar	9	4.25	58
EC	30	3–3.9 atm	52 <sup>(3)</sup>	3.25 <sup>(3)</sup>	59
CA	30	3–3.9 atm	15.2 <sup>(3)</sup>	2.6 <sup>(3)</sup>	59
PSF	30	3–3.9 atm	25 <sup>(3)</sup>	1.4 <sup>(3)</sup>	59
6FDA-mPD	35	3.8 atm	0.13	10	60
6FDA-IpDA	35	3.8 atm	0.58	15	60
6FDA-6FpDA	35	3.8 atm	0.89	16	60
6FDA-33'DMDB	35	1.1 atm	0.15	13.2	61
Matrimid	35	2 atm	0.10	10	61
6FDA-TeMPD	50	2 atm	37	8.6	62
6FDA-TrMPD	50	2 atm	30	11	62
6FDA-DDBT	50	2 atm	1.8	20	63
BPDA-TeMPD	50	2 atm	3.2	13	62
PPO	50	2 atm	2.3	9.1	62
P4MP	50	2 atm	54	2	62
1.2PB	50	2 atm	260	1.7	62
PDMS	50	2 atm	6600	1.1	62
6FDA-ODA	100	2 atm	0.48	11	62

1. A detailed chemical description of the abbreviations used for polymer materials is given in Abbreviations section

2. 1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cm Hg

3. Feed mixture: 55% propylene, 45% propane

tem. Their experimental results are summarized in Table 6.

### 3.1.1.2. 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 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 [64–66].

Kong and co-workers [67] used polyimide (PI)/TiO<sub>2</sub> nano composite membranes for gas separation. The permeation properties of these membranes are illustrated in Table 7. As it can be seen from these results, the low TiO<sub>2</sub> content could not greatly enhance the permeation properties of the composite membranes. When the TiO<sub>2</sub> content in the composite membranes was above

Table 7

Permeability (barrer) and selectivity of PI/TiO<sub>2</sub> composite membrane with different TiO<sub>2</sub> content [67]

TiO <sub>2</sub> content (wt%)	$P_{H_2}$	$P_{O_2}$	$P_{N_2}$	$P_{CH_4}$	$\alpha_{H_2/N_2}$	$\alpha_{H_2/CH_4}$	$\alpha_{O_2/N_2}$
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
10	4.696	0.199	0.045	0.030	104.3	157.6	4.4
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

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<sub>2</sub> component in PI/TiO<sub>2</sub> composite membranes. At TiO<sub>2</sub> content of 25wt%, the results were very interesting because both of the permeability and selectivity of PI membrane were enhanced at the same time.

Hu and co-workers [68] used fluorinated poly (amide imide) (6FPAI)/TiO<sub>2</sub> nano composite membranes for gas separation. The permeation properties of these membranes are summarized in Table 8. As it can be seen, the composite membrane has shown higher selectivities for selected gas pairs when compared to the pure poly (amide imide) membrane, even at very low volume concentration of the TiO<sub>2</sub> component. Such results are encouraging, because they suggest that possibly higher selectivities could be achieved at increasingly higher concentrations of the TiO<sub>2</sub> component.

Zhang and co-workers [69] 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 9. It could be seen that the nickel amount had strong influence on the gas permeation properties of the corresponding membrane.

Gomes and co-workers [70] used nano composite membranes based on poly (1-trimethylsilyl-1-propyne) (PTMSP) and organically modified silicates (ORMOSILs) for gas separation. In nano composite membranes different ORMOSILs were used such as: TEOS (tetraethoxysilane), OMDEOS (n-octylmethyldiethoxysilane), MTEOS (methyl triethoxysilane), OTEOS (n-octyltriethoxysilane), VTEOS (vinyltriethoxysilane), PTDMOS (phenethyl dimethoxysilane), DPDMS (diphenyldi-

Table 8

Permeability (barrer) and selectivity of 6FPAI/TiO<sub>2</sub> composite membrane with different TiO<sub>2</sub> content and at 35°C [68]

TiO <sub>2</sub> content (wt%)	$P_{CH_4}$	$P_{N_2}$	$P_{O_2}$	$P_{CO_2}$	$P_{H_2}$	$\alpha_{O_2/N_2}$	$\alpha_{CO_2/CH_4}$	$\alpha_{H_2/CH_4}$
0	1.80	2.30	11.2	52.7	67.0	4.9	29.3	37.2
7.3	1.30	1.80	9.2	44.7	66.2	5.0	33.3	50.8

Table 9

Single gas permeance ( $10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) and ideal selectivity of Ni-filled carbon membranes with different amounts of nano-sized nickel [69]

Ni content (wt%)	$P_{H_2}$	$P_{CO_2}$	$P_{O_2}$	$P_{N_2}$	$\alpha_{H_2/N_2}$	$\alpha_{CO_2/N_2}$	$\alpha_{O_2/N_2}$	$\alpha_{CO_2/H_2}$
0	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

methyloxysilane), PMDMOS (phenylmethyl dimethoxysilane). Permeation properties of single gases in these membranes are summarized in Table 10. From these data, it may be seen that both butane permeability and butane/methane selectivity of PTMSP-silica nano composite membranes could be increased by the incorporation of MTEOS in the membrane.

### 3.1.2. Liquid membranes

It is possible to use liquid as a membrane and the same general definition of a membrane also applies in this case: the liquid membrane or liquid film separates two phases from each other. Also here separation occurs because of differences

in solubility and diffusivity in the liquid film similar to a solid film. However, when a carrier is present inside the membrane with the ability to complex with a specific solute, the flux of that solute may be enhanced. The carrier may be dissolved in the liquid and in this case the carrier is mobile. On the other hand, the carrier can be bound chemically (covalently) or physically to a solid polymer. In this case, the carrier is fixed and has a very restricted mobility. In the mobile carrier system, which is referred to as ‘liquid membrane’, the carrier-solute complex diffuses across the membrane whereas in the fixed carrier system the solute jumps or hops from one site to the other. It is obvious that the diffusivity in the mobile system is much higher. Between these two limits, there is a large area where the continuous phase can be considered as a gel or a solvent swollen polymer and as a consequence the diffusivity will increase. In these systems, the carrier can either be fixed or mobile; however, when the carrier is fixed it still has a certain mobility compared to a carrier in an unswollen system.

The mobile carrier systems are referred to as liquid membranes. One of the benefits of using such membranes is that they are highly selective, and with the use of carriers for the transport mechanism, specific molecular recognition can be achieved [71–73]. The characteristic of a facilitated or carrier mediated transport in liquid membrane systems is the occurrence of a reversible chemical reaction or complexation process in

Table 10

Permeability (barrer) and selectivity of PTMSP/silica nano composite membrane with different silica content [70]

PTMSP membrane with ORMOSILs (molar ratio)	$P_{C_4H_{10}}$	$P_{CH_4}$	$\alpha_{C_4/CH_4}$
—	6120	780	8.1
1:1 TEOS/OMDEOS	990	120	8.3
1:1 TEOS/MTEOS	6280	495	12.7
1:1 TEOS/OTEOS	3850	280	13.9
1:1 TEOS/VTEOS	2320	205	11.3
1:1 TEOS/PTDMOS	1620	160	9.9
1:1 TEOS/DPDMOS	1350	130	10.2
1:1 TEOS/PMDMOS	2500	270	9.3

combination with a diffusion process. This implies that two cases can be distinguished:

- Diffusion is rate-limiting (fast reaction)
- Reaction is rate-limiting (slow reaction and relatively fast diffusion)

The latter case does not occur frequently and only the former case will be considered [11,74].

Carrier mediated transport has very large and various applications. Cations such as copper ( $\text{Cu}^{2+}$ ), mercury ( $\text{Hg}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ), cadmium ( $\text{Cd}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ) and lead ( $\text{Pb}^{2+}$ ), and anions such as nitrate ( $\text{NO}_3^-$ ) and chromate ( $\text{Cr}_2\text{O}_7^-$ ) can be easily removed via facilitated transport. Gases can also be removed by facilitated transport. Examples are the separation of oxygen from nitrogen, the removal of  $\text{H}_2\text{S}$  from natural gas,  $\text{NH}_3$ ,  $\text{NO}_x$  and  $\text{SO}_2$  from waste gases, separation of hydrocarbons and removal of phenol from waste water [11,75–82].

Because the carrier facilitated transport process employs a reactive carrier species, very high membrane selectivities can be achieved. These selectivities are often far larger than the selectivities achieved by other membrane processes. This one fact has maintained interest in facilitated transport for the past 30 years, but no commercial applications have developed. The principal problem is the physical instability of the liquid membrane and the chemical instability of the carrier agent. In recent years a number of potential solutions to this problem have been developed, which may yet make carrier facilitated transport a viable process [7,83,84].

There are three basic types of liquid membranes, which are presented schematically in Fig. 2 [85–91]:

- Bulk liquid membrane (BLM)
- Emulsion liquid membrane (ELM)
- Supported liquid membrane (SLM)
  - Thin sheet SLM
  - Hollow fiber SLM

In this section facilitated transport of olefin is

discussed in detail and liquid membrane systems used for the separation of olefin/paraffin are reviewed.

### 3.1.2.1. Facilitated transport of olefin in membrane

It is well known that some transition metals react reversibly with alkenes in the solution. The ability of the transition metal ion as a carrier is largely dependent on the intensity of the  $\pi$ -complexation with alkenes. The intensity of the  $\pi$ -complexation with alkenes is determined primarily by the electronegativity, which is a measure of the relative strength of an atom in a molecule to attract bonding electrons to itself. The electronegativity values of transition metals are presented in Table 11 [92]. With the greater electronegativity, the metal atom draws bonding electrons more strongly. If the electronegativity of the metal is excessively high, the metal is not suitable for the facilitated carrier because it is susceptible to irreversible reaction with the electrons of the alkene; otherwise, if the electronegativity is too low, the metal is impractical as a carrier due to its weak interaction with the alkene. For reversible reaction between the transition metal ion and the alkene, the electronegativity of the metal is preferably in the range of 1.6–2.3. Examples of the suitable transition metal from Table 11 may include Mn, Fe, Co, Ni, Cu, Mo, Tc, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt.

To increase the reversible reactivity of the transition metal ion with the alkene, the anion of the transition metal plays an important role in determining the intensity and the rate of the interaction between a carrier and alkene. In order for the transition metal to act as a carrier, the transition metal salt is solvated on the polymer to form a complex.

With the lower lattice energy of the transition metal salt, the anion form a weak ionic bond or ion pair with the cation and the salt is easily dissolved in a polymer. It is therefore preferable to

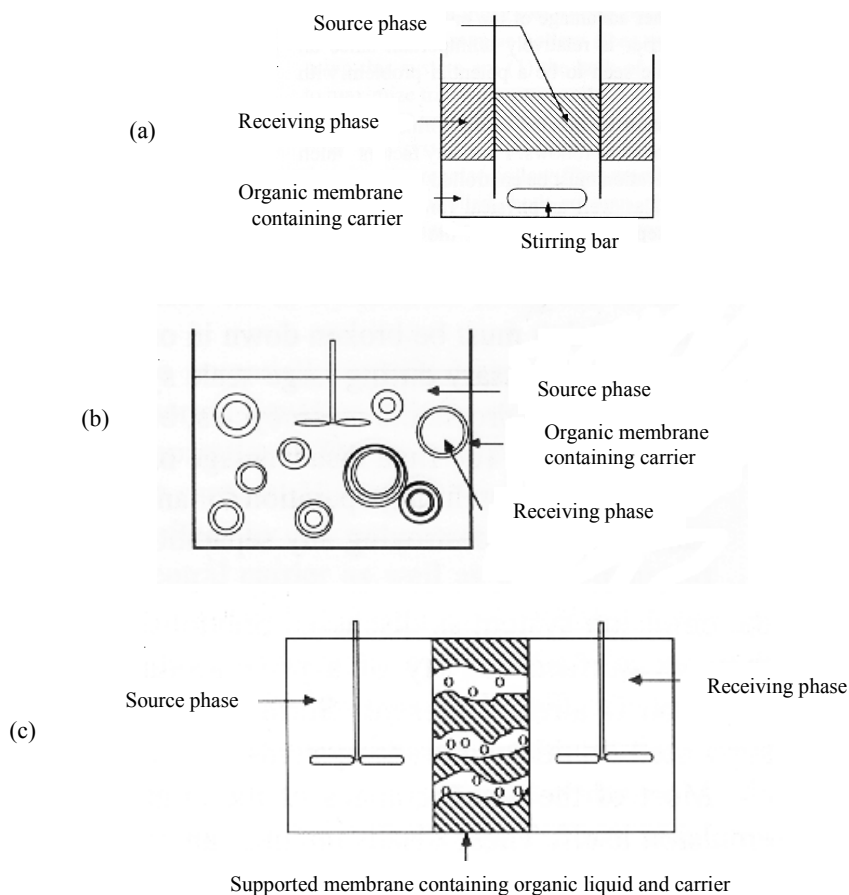


Fig. 2. Schematic setup of liquid membranes: (a) bulk liquid membrane (BLM), (b) emulsion liquid membrane (ELM), (c) thin sheet supported liquid membrane (thin sheet SLM).

Table 11  
The electronegativity values of transition metals [92]

Transition metal	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electronegativity	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9
Transition metal	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Electronegativity	1.3	1.3	1.6	2.2	1.9	2.2	2.3	2.2	1.9
Transition metal	La	Hf	Th	W	Re	Os	Ir	Pt	Au
Electronegativity	1.0	1.3	1.5	2.4	1.9	2.2	2.2	2.3	2.5

Table 12  
Lattice energy of metallic salts (kJ/mole) [92]

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ag <sup>+</sup>	Cu <sup>+</sup>	Co <sup>2+</sup>	Mo <sup>2+</sup>	Pd <sup>2+</sup>	Ni <sup>2+</sup>	Ru <sup>3+</sup>
F <sup>-</sup>	1036	923	823	967	1060	3018			3066	
Cl <sup>-</sup>	853	786	715	915	996	2691	2733	2778	2772	5245
Br <sup>-</sup>	807	747	682	904	979	2629	2742	2741	2709	5223
I <sup>-</sup>	757	704	649	889	966	2545	2630	2748	2623	5222
CN <sup>-</sup>	849	739	669	914	1035					
NO <sub>3</sub> <sup>-</sup>	848	756	687	822	854	2626			2709	
BF <sub>4</sub> <sup>-</sup>	705	619	631	658	695	2127			2136	
ClO <sub>4</sub> <sup>-</sup>	723	648	602	667	712					
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	779	685	600	719	793					
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	822	726	658	782	848					

select the anion of the transition metal salt that has low lattice energy with respect to the cation of the transition metal, in order to facilitate the solvation of the transition metal salt. The lattice energies of the representative transition metals are presented in Table 12.

In the facilitated transport membrane, the transition metal salt preferably has lattice energy of less than 2500 kJ/mol, reducing the tendency of the anion of the transition metal salt to form a strong ion pair with the cation. Among the metal salts listed in Table 12, the suitable anion may include F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> or CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>.

The tendency of the anion to form a strong ion pair with the cation decreases in the order of F<sup>-</sup> << Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup> ≈ SCN<sup>-</sup> < ClO<sub>4</sub><sup>-</sup> ≈ CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> < BF<sub>4</sub><sup>-</sup> ≈ AsF<sub>6</sub><sup>-</sup>, with a decrease in the lattice energy [92].

Facilitated transport of olefin is shown in Fig. 3. Olefin is complexed with a complexing agent B such as Ag<sup>+</sup> incorporated in the membrane at high-pressure side. The complex diffuses owing to its concentration difference across the membrane from the high-pressure side to the low-pressure side, where decomplexation takes place to release the olefin. The complexing agent regenerated from the decomplexation, diffuses back to the high-pressure side due to its concentration difference between the low- and high-pressure

sides. This completes a facilitated transport cycle, and the complexing agent repeats the cycles. Because of the complexation, the concentration of the olefin in the membrane is increased, and the transport of the olefin is thus facilitated. On the other hand, paraffin cannot complex with the complexing agent, and the majority of the paraffin is thus rejected by the membrane. The concentration of the paraffin in the membrane is small by physical solubility, and its transport rate through the membrane is thus low. Therefore, the facilitated transport membrane can give a high olefin/paraffin selectivity to yield a permeate with high olefin purity [93,94].

### 3.1.2.2. Olefin/paraffin separation using liquid membrane systems

In order to improve the performance of polymeric membranes, it is possible to incorporate silver salts in the membrane system, since it has a facilitation effect [95–100]. During 1993–1997, BP-Amoco had successfully developed a high efficiency process for the separation of light olefins from the corresponding paraffins using facilitated transport and micro-porous polypropylene hollow-fiber contactors. They used silver nitrate as complexing agent for facilitation transport and they did the separation experiments in

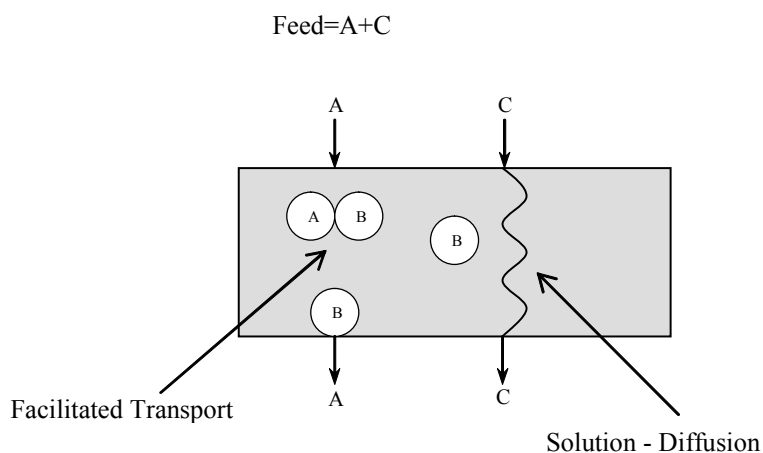


Fig. 3. Facilitated transport mechanism in membrane separation [93]. A = olefin, B = carrier, C = paraffin.

bench-scale and pilot plant [101]. In Table 13 different membrane systems with various polymers and silver salts for the separation of propylene-propane mixtures are reviewed.

In order to improve the performance of polymer-silver salt complex membranes, some researchers used a third component in the membrane system. An overview of these membrane systems can be found in literature [102–123].

### 3.2. Liquid separation by membranes

In this section, separation of light solvents and solvent dewaxing by a membrane system are reviewed. Petrochemical waste streams may contain phenolic compounds or aromatic amines. They are highly toxic and at high concentrations are inhibitory to biological treatment. Membrane aromatic recovery system (MARS) which is a relatively new process for recovery of aromatic acids and bases is described, and finally, the application of membrane in the delivering/receiving stations with the aim of emission control is investigated.

#### 3.2.1. 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 by Binning and co-workers 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 Fig. 4. 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.



Table 13  
 $C_3H_6/C_3H_8$  permeation data in polymer–silver salt complex membranes

Membrane <sup>1</sup>	Mole fraction of Ag	Selectivity	Permeance (GPU <sup>2</sup> )		Reference
			Propylene	Propane	
PVP/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	10000 <sup>(3)</sup>	31 <sup>(3)</sup>	0.0031 <sup>(3)</sup>	124
PMMA/AgBF <sub>4</sub>	0.5	40 <sup>(4)</sup>	—	—	125
PMMA/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	18 <sup>(4)</sup>	—	—	125
PBMA/AgBF <sub>4</sub>	0.5	35 <sup>(4)</sup>	—	—	125
PBMA/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	14 <sup>(4)</sup>	—	—	125
PVMK/AgBF <sub>4</sub>	0.5	54 <sup>(4)</sup>	—	—	125,126
PVMK/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	15 <sup>(4)</sup>	—	—	125
PVP/AgBF <sub>4</sub>	0.5	50 <sup>(4)</sup>	—	—	125
PVP/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	15 <sup>(4)</sup>	—	—	125
POZ/AgBF <sub>4</sub>	0.5	48 <sup>(4)</sup>	—	—	125
POZ/AgCF <sub>3</sub> SO <sub>3</sub>	0.5	17 <sup>(4)</sup>	—	—	125
POZ/AgCF <sub>3</sub> SO <sub>3</sub>	0.8	25000 <sup>(3)</sup>	50 <sup>(3)</sup>	0.002 <sup>(3)</sup>	127
PVP/AgCF <sub>3</sub> SO <sub>3</sub>	0.8	17333 <sup>(3)</sup>	52 <sup>(3)</sup>	0.003 <sup>(3)</sup>	127
PEOx/AgBF <sub>4</sub>	1	58 <sup>(4)</sup>	34 <sup>(4)</sup>	—	128
PEOx/AgCF <sub>3</sub> SO <sub>3</sub>	1	17 <sup>(4)</sup>	32 <sup>(4)</sup>	—	128
PVP/AgBF <sub>4</sub>	1	68 <sup>(4)</sup>	35 <sup>(4)</sup>	—	128
PVP/AgCF <sub>3</sub> SO <sub>3</sub>	1	15 <sup>(4)</sup>	28 <sup>(4)</sup>	—	128
PVA/AgSbF <sub>6</sub>	0.2	130	4	0.03	129
CA/AgBF <sub>4</sub>	0.75	200 <sup>(4)</sup>	—	—	130
PAAm/AgBF <sub>4</sub>	0.67	170 <sup>(4)</sup>	—	—	55

1. A detailed chemical description of the abbreviations used for polymer materials is given in Abbreviations section

2. 1 GPU = 10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup> s cm Hg

3. Permeances are for “pure propylene” and “pure propane” and selectivity is “ideal selectivity”

4. Permeances are for feed mixture [propylene: propane = 50 : 50 (vol %)]

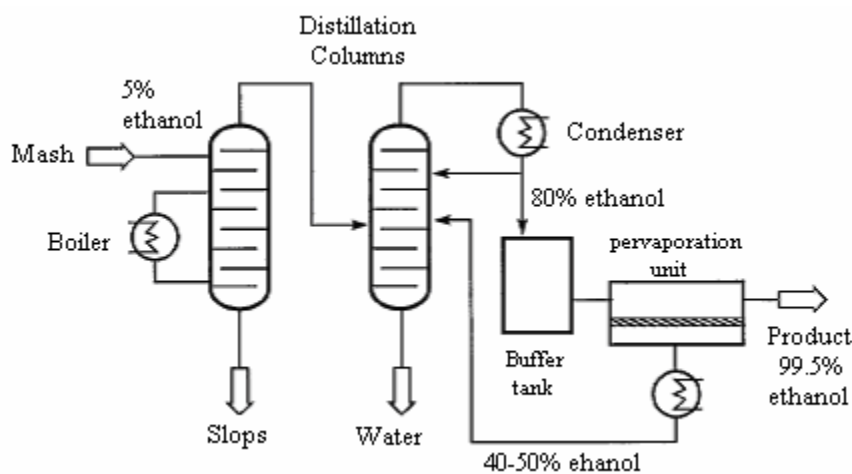


Fig. 4. Flow scheme of a GFT plant for ethanol recovery [131].



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 [2,7].

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 [131, 11].

### 3.2.2. 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. Nonetheless, this is an area of keen industrial interest, and from 1988 to 1998 more than 30 US patents covering membranes and membrane systems for these applications were issued.

One application that has already reached the

commercial stage is the separation of small solvent molecules from larger hydrocarbons in mixtures resulting from the extraction of vacuum residual oil in refineries [132,133]. Fig. 5a shows a simplified flow diagram of a refining lube oil separation process — these operations are very large. In a typical 100,000 barrel/d refinery about 15,000 barrel/d 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 3–10 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 was developed by Mobil for this separation which is illustrated in Fig. 5b. 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 10–20 gal/ft<sup>2</sup>d at a pressure of 450–650 psi. The solvent filtrate bypasses the distillation step and is recycled directly to the incoming oil feed. The net result is a significant reduction in the refrigeration load required to cool the oil and in the size and energy consumption of the solvent recovery vacuum distillation section.

Mobil is now licensing this technology to other refineries. Development of similar applications in other operations is likely. Initially, applications will probably involve relatively easy separations such as the separation of methyl ethyl ketone/toluene from lube oil described above or soybean oil from hexane in food oil production. Long term, however, the technology may become sufficiently advanced to be used in more important refining operations, such as fractionation of linear from branched paraffins, or the separation of benzene and other aromatics from paraffins and olefins in the gasoline pool [134].

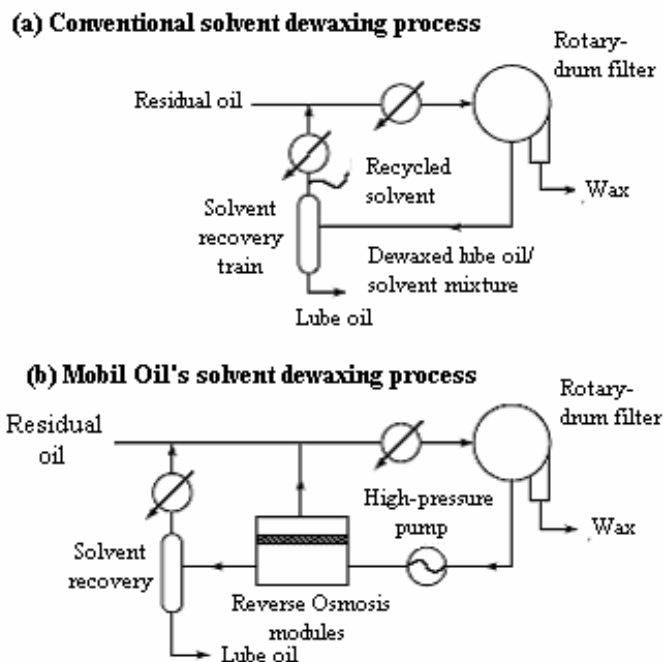


Fig. 5. Simplified flow schemes of (a) a conventional and (b) Mobil Oil's membrane solvent dewaxing processes [135].

### 3.2.3. Phenol and aromatic recovery

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 [136].

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 [137].

Since phenol is highly toxic and at high concentration (>200 mg/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 [138].

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 [139–142]. 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  $\mu\text{m}$ . 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. The operating principle of MARS for recovery of phenolic compounds is shown in Fig. 6 [143].

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 [143].

MARS technology has been successfully applied for the recovery of phenol and aniline at lab and pilot plant scale [136]. It has also been applied on full plant scale for recovery of p-cresol since December 2002 at Degussa plant in Knottingly UK [139].

#### 3.2.4. Control emission at delivering-receiving stations

A spin-off of the activities of gasoline vapor recovery at gasoline tank farms is the development of a system to reduce emissions generated by the operation of petrol stations. In the case of car 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. In order to avoid the emission transfer from the tank filling point of the car to

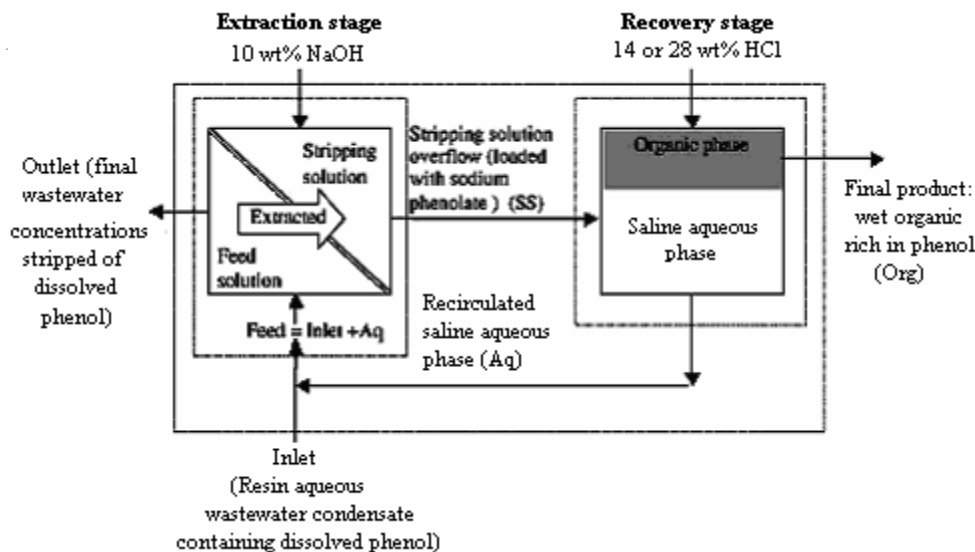


Fig. 6. The operating principle of MARS for recovery of phenolic compounds [137].

the vent pipes of the storage tanks, an air over liquid ratio of 1:1 of the vapor return system has been stipulated. An investigation of the TÜV Rheinland has shown that the efficiency of catching emissions by means of the 1:1 vapor return ratio is limited to an average of approx. 75%. 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, e.g. 6 mbar, the vacuum pump of a membrane separation system is activated. This system is installed parallel to the vent stack of the storage tanks. A pneumatic valve in the retentate line of the membrane module is opened by the applied vacuum. The overpressure of the storage tanks causes a volume flow, which is released by passing the membrane stack. The gasoline vapors are separated from the off-gas and clean air enters to the atmosphere. After the lower set point of the pressure gauge, e.g. 3 mbar, is reached, the system is deactivated (Fig. 7). Besides the advantage of emission reduction, the wet stock losses of gasoline storage can be reduced

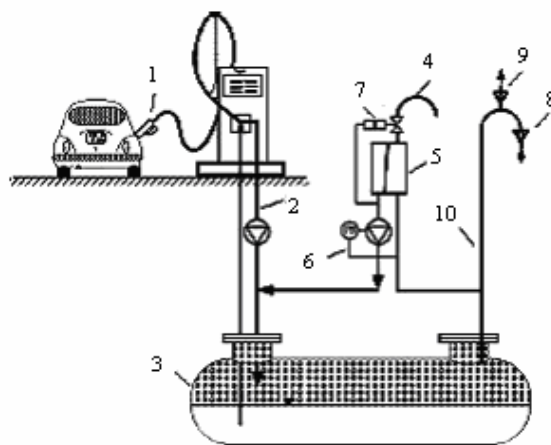


Fig. 7. Control emissions at receiving stations [144]. 1 petrol pump with vapor return nozzle, 2 vapor return line, 3 horizontal tank, 4 stack, 5 membrane module, 6 vacuum pump with pressure switch, 7 pneumatic valve, 8 air intake valve, 9 air outlet valves, 10 Breather pipe.

because diffusive emissions are avoided and most of the generated gasoline vapor is returned to the storage tank [144].

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.

#### 4. Membrane reactors

Membranes are mainly used for concentration, purification and fractionation. However, they may be coupled to a chemical reaction to shift the chemical equilibrium and the combination is defined as a membrane reactor. In this case one of the end products is removed to shift the reaction to the right side and consequently the conversion rate or final product concentration has been enhanced. The final result is an improvement of the productivity. Moreover, in most cases a purification step occurs as well, which makes a combination of reaction and purification. Also from an en-

ergy point of view, it is more favorable than conventional processes [11,145,146].

The concept of combining membranes and reactors is being explored in various configurations, which can be classified in three groups, regarding the role of the membrane in the process. The membrane can act as an extractor (the removal of product(s) increases the conversion by shifting the reaction equilibrium), as a distributor (the controlled addition of reactant(s) along the reactor wall limits side reactions), or as an active contactor (the controlled diffusion of reactants to the catalyst can lead to an engineered catalytic reaction zone). In the two first cases the membrane has usually no catalytic properties and is combined, for example, with a fixed bed of catalyst placed on one membrane side. In the active contactor mode, the membrane acts as a diffusion barrier and plays the role of a catalyst whereas separation properties are usually not required. The concept can be used with a forced flow-mode or with an opposing reactant mode. The forced flow contactor mode has been applied to the total oxidation of VOC. The distributor mode is usually well adapted to limit consecutive and parallel deep oxidation reactions for partial oxidation, oxidative dehydrogenation of hydrocarbons and oxidative coupling of methane. For these reactions, the local oxygen concentration at the catalytic site greatly influences both hydrocarbon conversion and product selectivity [147–152].

A membrane is going to add cost to any process, so for it to be cost effective, it must give one other advantage that outweigh the added cost. The original driving force behind catalytic membrane reactors is often to reduce the number of units concerned. To do so, one cannot substitute it with more expensive or exotic methods of separation. There are critical operational features of a membrane that one needs to be successful. These include:

- A material with a very good separation factor (small values such as 1.1, 2.2 are not going to drive one to spend the extra cost). Separation

factors of > 5 or approaching infinity are what one will ultimately need.

- High flux (rate of flow of permeating species per unit area of membrane surface).
- High quality membrane materials: the membrane material must be stable over many months of operation and the working layer must be flawless.

Inorganic or organic membranes can be used in a membrane reactor. The advantages of inorganic membranes have been recognized for a long time. Thermal and pH resistance characteristics of inorganic membranes are the most important advantages. The operable temperature limits of inorganic membranes are obviously much higher than those of organic polymeric membranes. The majority of organic membranes begin to deteriorate structurally around 100°C. Thermal stability of membranes is becoming not only a technical problem but also an economical issue. In gas separation applications, for example, if the membrane can withstand the required high process temperatures, the need to ramp down the temperature to maintain the physical integrity of an organic membrane and to ramp up the temperature again after separation, can be eliminated.

Inorganic membranes generally can withstand organic solvents, chlorine and other chemicals better than organic membranes. This also permits the use of more effective and yet corrosive cleaning procedures and chemicals. Many organic membranes are susceptible to microbial attack during applications. This is not the case with inorganic types, particularly ceramic membranes. In addition, inorganic membranes in general do not suffer from the mechanical instability of many organic membranes where the porous support structure can undergo compaction under high pressures and cause decrease in permeability. It is obvious that in a high temperature or harsh chemical environment, inorganic membranes could become the only recourse to many challenging separation applications.

Another very important operating characteristic of inorganic membranes is the phenomena of fouling and concentration polarization. Concentration polarization is the accumulation of the solutes, molecules or particles retained or rejected by the membrane near its surface. It is deleterious to the purity of the product and the decline of the permeate flux. Fouling is generally believed to occur when the adsorption of the rejected components on the membrane surface is strong enough to cause deposition. How to maintain a clean membrane surface so that the membrane can be continuously used without much interruption has been a key operational issue with many membranes. First of all some inorganic membranes such as microporous alumina membranes and surface treated porous glass membranes are more fouling resistant due to their low protein adsorption. Secondly, many inorganic membranes are less susceptible to biological and microbial degradation. And finally with some inorganic membranes, for example porous ceramic and metallic membranes, it is possible to apply short bursts of permeate streams in the reverse direction through the membrane to dislodge some clogged pores of the membrane. This is referred to as back flush. This way the maintenance cycle of the membrane system can be prolonged. Because of the unique characteristics of inorganic membranes mentioned above, the search for inorganic membranes of practical significance has been continuing for several decades.

Organic polymer membranes can only withstand relatively mild conditions such as those prevailing in biocatalysts involving enzymes and microorganisms and in some areas of homogeneous catalysis. Thus early studies of membrane reactors mostly dealt with low temperature reactions or enzyme-catalyzed biotechnology applications such as saccharification of celluloses and hydrolysis of proteins.

Many catalytic processes of industrial importance, however, involve the combination of high temperature and chemically harsh environments,

a factor that strongly favors inorganic membranes. So with the introduction of commercially available glass, ceramic and metal membranes, there has been a dramatic surge of interest in the field of membrane reactor or membrane catalysis. Some promising applications using inorganic membranes include certain dehydrogenation, hydrogenation and oxidation reactions such as formation of butadiene from butane by dehydrogenation, styrene production from dehydrogenation of ethyl benzene, dehydrogenation of ethane to ethene, water-gas shift reaction and oxidative coupling of methane, to name just a few [153].

In membrane reactor two basic concepts can be distinguished as illustrated by the reaction  $A \rightleftharpoons B$ :

- Reaction and separation are combined in one unit (Fig. 8a)
- Reaction and separation are not combined and the reactants are recycled along a membrane system (Fig. 8b)

The former concept is used especially in combination with inorganic membranes (ceramics, metals) and with polymeric membranes where the catalyst is coupled to the membrane. The latter concept can be applied with any membrane process and type of membranes, organic and inorganic. In fact any membrane process can be applied to remove a specific component such as microfiltration, ultrafiltration, nanofiltration, gas separation, vapor permeation, pervaporation, membrane distillation, electro dialysis, dialysis, diffusion dialysis, membrane contactors and facilitated type of processes.

Most chemical reactions are equilibrium and employ a catalyst to enhance the kinetics. The compounds involved in the reactions are either liquid or gaseous. In the latter case the temperature is often higher. Furthermore, the conversion is often strongly temperature dependant, which implies that each specific reaction is carried out at a specific temperature which is often higher than room temperature.



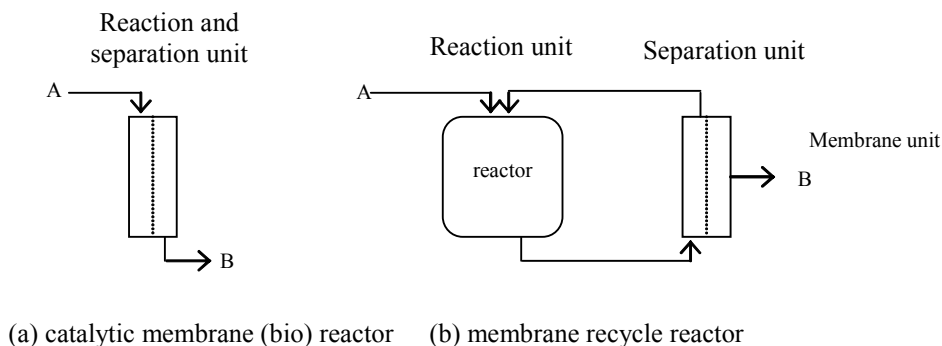


Fig. 8. Two concepts of a membrane reactor [11]: (a) reaction and separation are coupled in one unit (catalytic membrane reactor); (b) reaction unit and membrane unit are separated (membrane recycle reactor).

The catalyst must be combined with the membrane system and various arrangements are possible. Fig. 9 summarizes some membrane-catalyst combinations for tubular membranes [11].

The most simple and straightforward system is where the catalyst is located inside the bore of the tube (Fig. 9a). The advantage of this system is its simplicity in preparation and operation and in case of catalyst poisoning a new catalyst can easily be introduced. In the other two arrangements the catalyst is immobilized onto the membrane, either in the top layer (Fig. 9b) or in the membrane wall (Fig. 9c). In either case one of the products, not necessarily the required product, should permeate across the membrane which implies the necessity of permselective membranes under these specific conditions. At certain concentrations or partial pressures and at a certain temperature and pressure the equilibrium is completely fixed and thermodynamically determined. However, by removing one of the end products the reaction is shifted to the right hand side and results in an enhanced conversion rate.

Also the controlled addition of a reactant may enhance the productivity. Membrane processes are well suited to remove either a gaseous or liquid compound. Furthermore, they can be made catalytically active and employed at increased tem-

peratures by employing proper materials, i.e. inorganic materials such as ceramics, zeolites or metals.

Typical examples for inorganic membrane reactors are dehydrogenation, where hydrogen is removed and oxidation and hydrogenation where oxygen and hydrogen are added and some of these are summarized in Table 14 [11,145,154–156].

The number of possible applications is large but the commercial applications are emerging slowly due to a number of practical limitations such as low separation factor, leakage at higher temperatures, poisoning of catalyst and mass transfer limitations [11].

Many membrane reactors are demonstrated by using a sweep gas or a vacuum to assist in the permeation of a species, but in a commercial operation those will not be acceptable; ultimately, one has to be able to drive the separation with a method which does not dilute the permeating product (thus losing one of the key attributes of a membrane) or demand high energy input to perform additional separation.

#### 4.1. Membrane chemical reactors

In this section, membrane chemical reactors for processes such as dehydrogenation, oxidative

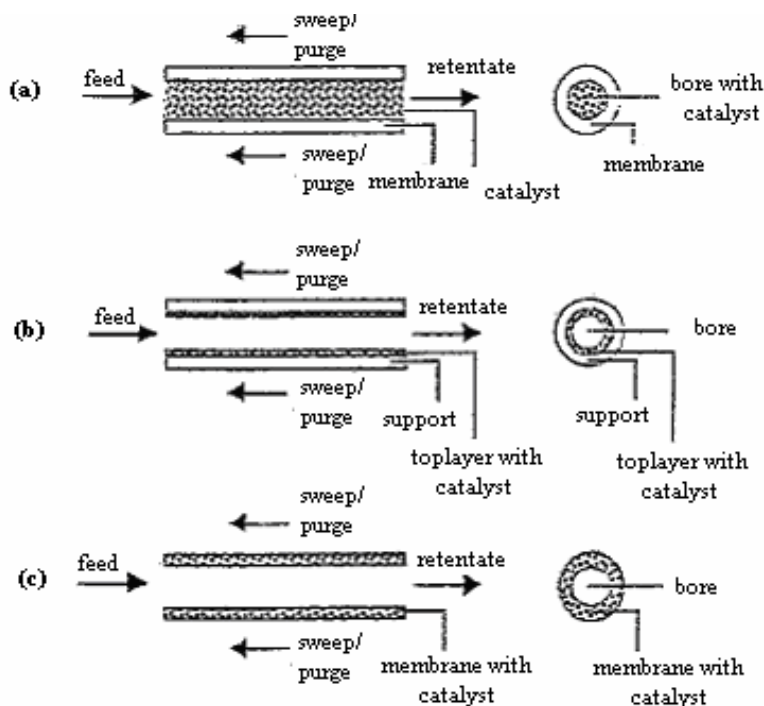


Fig. 9. Schematic drawing of various membrane reactor concepts for a tubular configuration [11]: (a) bore of the tube filled with catalyst; (b) top layer filled with catalyst; (c) membrane wall filled with catalyst.

coupling of methane, steam reforming of methane and water-gas shift reaction, which are important to petrochemical industry are discussed.

#### 4.1.1. Dehydrogenation

One of the most important petrochemical reactions by which hydrogen is produced, is dehydrogenation. Some of the dehydrogenation reactions frequently used in petrochemical industry are summarized in Table 14 and will be reviewed below.

For the dehydrogenation of cyclohexane to benzene, Itoh [157] used a 0.05 in thick Pd/Ag membrane tube containing a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to achieve 99% conversion. In this membrane reactor, an argon sweep gas was used to carry away the H<sub>2</sub> permeating through the Pd mem-

brane. The reaction over the catalyst was run at 200°C and 1 atm, using an argon stream saturated with cyclohexane vapor. In order to achieve substantial conversion, the actual feed rate over the catalyst had to be maintained very low and residence times ranged from 2.5 to 14.5 min. Space time yields of benzene were 0.0126 mole of benzene/kg catalyst/h, which corresponds to about 1 gr benzene/kg catalyst/hr (about 1000 times lower than the commercial catalyst units) [157, 158].

Kikuchi and co-workers [159–162] used a Pd alloy coated onto a mesoporous membrane support for the dehydrogenation of isobutane. In their study, isobutane was passed over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst contained within the membrane. The yield of isobutylene rose from the equilibrium value of 6% (demonstrated in the absence of a membrane) to 23% at 400°C with this membrane.



Table 14  
Reactions in catalytic membrane reactors

Dehydrogenation	Ethane → ethylene
	Propane → propylene
	Cyclohexane → benzene
	Cyclohexane → cyclohexene
	ethylbenzene → styrene
	Butane → butadiene
	Isopropylalcohol → acetone
Isobutane → isobutylene	
Hydrogenation	Propene → propane
	Butene → butane
	Ethylene → ethane
Oxidation	Carbon monoxide → carbon dioxide
	Ethylene → ethylene oxide
	Propylene → propylene oxide

For the dehydrogenation of propane, Brinker and co-workers [163] used a Pd film coated on a mesoporous  $\text{Al}_2\text{O}_3$  support. Propylene yields rose from the equilibrium value of 30% (in the absence of a membrane) to 40% at 550°C.

Reforming via dehydrocyclization of heptane is another dehydrogenation reaction. Ali and Baiker [164] used a system of two plug flow reactors with an interstage Pd/Ag membrane for *ex situ*  $\text{H}_2$  separation from the product stream of the first reactor using a commercial Pt/ $\text{Al}_2\text{O}_3$  catalyst for toluene production. With this system, at 400°C and 17 atm, 65% higher toluene yield was obtained.

Ethylbenzene dehydrogenation to styrene is another worthy of mention dehydrogenation reaction in petrochemical industry. Liu and co-workers [165] studied a two stage packed bed reactor followed by a membrane reactor. The tubular 40°A alumina mesoporous membrane was packed with a commercial K promoted iron oxide catalyst used for styrene production. In this system, a 4% yield enhancement to styrene was observed.

Liang and Hughes [166] used a palladium/silver membrane reactor, containing a platinum catalyst within the membrane tube, for the dehydrogenation of isobutane to isobutene. For a temperature of 485°C at a residence time of 3.5 s, using 100 ml/min of sweep gas ( $\text{N}_2$ ), the yield was 15% and using 1000 ml/min of sweep gas ( $\text{N}_2$ ), the yield was 20%. At a higher temperature of 520°C and residence time of 3.5 s, the yield of isobutene was 22% and 29% for the 100 ml/min and 1000 ml/min of sweep gas ( $\text{N}_2$ ).

Bobrov and co-workers [167] investigated the propane dehydrogenation using inorganic membranes with molybdenum (Mo) selective layer. The maximum selectivity to propylene for Mo-ceramic membrane (Mo coated on ceramic support) was 63% (at 853 K and conversion to propane 17%). The maximum selectivity to propylene for Mo-carbon membrane (Mo coated on carbon support) was 84% (at 853K and conversion to propane 28%).

Sznejder and Sheintuch [168] used a membrane reactor, equipped with a molecular-sieve carbon membrane, for isobutane dehydrogenation on a chrome alumina catalyst. Two types of operation mode were studied, using nitrogen as a sweep gas in counter-current flow or using vacuum as a driving force for membrane transport. At 500°C, in counter-current flow operation, the conversion of 85% was obtained and in the vacuum mode, the conversion of 40% was obtained.

Ahchieva and co-workers [169] studied the performance of a fluidized bed membrane reactor (FLBMR) for the catalytic oxidative dehydrogenation of ethane using  $\gamma$ -alumina supported vanadium oxide catalyst. The experimental results were compared to the conventional operation such as fluidized bed reactor (FLBR). Ethylene selectivity is higher in the FLBMR (up to 20%) than in the FLBR. The maximum ethylene yield observed was 36.6% for the FLBMR and 23.3% for the FLBR. It means FLBMR performance is near 1.6 times higher than that of the FLBR.

#### 4.1.2. Oxidative coupling of methane (OCM)

With depletion in liquid petroleum, natural gas containing primarily methane (>95%) is increasingly expected to be one of the main resources for production of chemicals and liquid fuels. So far, there are mainly two different methods that have been studied in converting methane to chemicals and liquid fuels, namely, direct or indirect routes. The direct route is the oxidative coupling of methane (OCM) into  $C_2$  products (ethane and ethylene), and the indirect route is the production of syngas ( $H_2$  and CO mixture) by steam reforming or partial oxidative reaction of methane followed by a further conversion into higher hydrocarbons by the Fischer–Tropsch process. Comparatively, the direct route is economically more promising if the  $C_2$  yield can be remarkably improved. Because the  $C_2$  products from the OCM reaction are more reactive in nature than the starting reactant (methane), they are easily deep oxidized, leading to low selectivities. Therefore, the inherent limit to  $C_2$  yields in conventional catalyst packed-bed reactors is around 25%. To achieve an economically attractive  $C_2$  yield (> 30–40%), considerable interests have been recently devoted to the development of various membrane reactors. By the addition of oxygen discretely through a membrane along the length of the reactor, the local methane-to-oxygen ratio in the reaction zone can be kept high so that a much higher  $C_2$  selectivity than that in a conventional reactor can be obtained. As a result, the  $C_2$  yield can be greatly increased once the total amount of oxygen introduced into the reactor is high enough for methane conversion [170].

There are two types of membrane reactors that have been studied for OCM over the past decade: (1) porous ceramic membrane reactors and (2) dense ionic or mixed-conducting oxide membrane reactors. In general, the porous membranes such as alumina, zirconia, or Vycor glass have high stability for the reactions but low oxygen selectivity. However, for the dense ionic or mixed-con-

ducting oxide membranes, the oxygen selectivity is theoretically infinite, and thus air can be used as an oxygen source without contaminating the products with nitrogen and nitrogen oxides. In addition, some oxides such as  $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$  and  $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$  also exhibit noticeable catalytic activity for OCM, this would further promote the formation of  $C_2$  products.

Although  $C_2$  selectivities up to 90–95% have been reported for OCM in dense ceramic membrane reactors, the  $C_2$  yields are generally low (between 1 and 10%) because of the low oxygen permeation flux. This suggests that efforts should be placed in improving the oxygen permeation flux of the mixed-conducting membranes so as to achieve a high  $C_2$  yield. In most studies, disk-shaped membranes with a limited membrane area (<5 cm<sup>2</sup>) have been employed to perform OCM. Such membranes obviously fail to provide enough oxygen for methane conversion. Recently, tubular dense membranes have been developed for OCM, resulting in a much higher  $C_2$  yield. However, the small surface area/volume ratio and the relatively high membrane thickness that would lower the oxygen permeation rate make them unfavorable in practical applications. Recently, hollow-fiber ceramic membranes with an asymmetric structure (i.e. a thin dense and separating layer integrated with a porous substrate of the same material) have been used. Compared to disk-shaped membranes, such hollow-fiber membranes possess much larger membrane area per unit volume values for oxygen permeation. All of these advantages of the hollow-fiber ceramic membrane, i.e. the asymmetric structure and hollow-fiber geometry, are beneficial in commercializing mixed-conducting membrane reactors for OCM.

In a novel membrane reactor for OCM where a dense semi-permeable ionic conductor is used, the contact mode of oxygen and methane is controlled. Two approaches have been reported using these types of membrane reactors to improve the selectivity and yield of OCM. In the first ap-

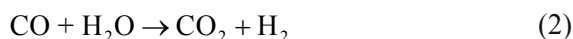
proach, the membrane is used as the oxygen separator (if the air is used as the reactant) and oxygen distributor [171,172]. The other approach requires that the surface of the oxygen semi-permeable membrane is catalytically active and selective for OCM. In this case oxygen permeates through the membrane and reacts, in the form of non-molecular oxygen, with membrane on the other surface of the membrane. This approach minimizes the amount of the gas-phase oxygen in the membrane stream, therefore reducing the total oxidation reactions in the gas phase.

Table 15 summarizes the work published on the second approach for OCM. The membranes used in these studies were made of both perovskite and fluorite type materials. In most cases, the membrane surface is not modified with other catalysts except for the work reported by Nozaki and Fujimoto [173] and Guo and co-workers [174]. Most reactors employed disk-shaped perovskite type ceramic membranes and offered very low  $C_2$  yields (<4%) because of the low surface activity of the membrane material and unfavorable disk geometry of the membrane. Among the perovskite type ceramic membrane reactors, the highest  $C_2$  yield (16.5%) was obtained by Lu and co-workers [175] using a tubular  $BaGe_{0.8}Gd_{0.2}O_3$  membrane. Zeng and co-workers [176] optimized the methane-to-helium ratio and showed that a perovskite type  $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$  membrane was more active and selective for OCM under the conditions of p-type electronic conduction. The OCM activity ( $C_2$  formation rate) for a  $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$  membrane reported by Zeng and co-workers is an order of magnitude higher than that for the  $BaGe_{0.8}Gd_{0.2}O_3$  membrane surface reported by Lu and co-workers. However, the latter (in tubular geometry) offers a higher  $C_2$  yield than the former (in disk geometry). This result suggests that the membrane geometry has a strong effect on the performance of the membrane reactor. However, a strict comparison could not be made on these two membrane reactors because the membrane materials were different.

The results summarized in Table 15 also show that fluorite-structured bismuth oxide based membranes are catalytically very active and selective for OCM. The surface activity of the bismuth oxide based membranes is about 2 orders of magnitude higher than those of most perovskite type ceramic membranes studied. The  $C_2$  yields for the membrane reactors made of the disk-shaped bismuth oxide membranes are comparable to the tubular perovskite type membranes reported by Lu and co-workers. The results on the perovskite type ceramic membrane reactors suggest that the membrane in tubular geometry is more favorable for obtaining higher yield.

#### 4.1.3. Steam reforming of methane (SMR)

Hydrogen and syngas (a mixture of CO and  $H_2$ ) are more economically produced nowadays by steam reforming of methane. As  $CH_4$  is a stable hydrocarbon, extremely high reaction temperatures and pressures, around 800°C and 20atm are required for endothermic reaction (1). Carbon monoxide is further reformed with steam to  $CO_2$  and  $H_2$  by exothermic reaction (2).



If  $H_2$  is selectively removed from the reaction system, thermodynamic positions of these reactions are shifted to the product sides and highly efficient conversion of  $CH_4$  to  $CO_2$  and  $H_2$  can be attained and it can be accomplished even at low temperatures. Selective removal of hydrogen in a membrane reactor enabled the hydrogen production by steam reforming at lower reaction temperatures than conventional processes [184].

By using a Pd alloy membrane which is packed with traditional SMR catalyst, the interest is to shift the reaction to produce more  $H_2$  at lower operating temperatures. This membrane would also produce pure  $H_2$  thus eliminate extensive  $H_2$  purification steps [185].

Table 15  
Summary of works done on OCM using catalytically active dense ceramic membrane reactors

Membrane	Configuration	Temp. (°C)	S (%)	Y (%)	C <sub>2</sub> formation rate (μmole/m <sup>2</sup> .s)	Reference
Porous SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (1:2) with PbO-K <sub>2</sub> O-coated dense layer	Tubular, $w = 0.1$ mm (coating layer)	800	~90	0.2 – 0.3	~1	173
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	Disks with $w = 0.5$ – $2.0$ mm and $\phi = 15.2$ mm	880	67	~ 1.5	~ 0.24	177
La <sub>0.8</sub> Ba <sub>0.2</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>		880	56		~ $0.2 \times 10^{-1}$	177
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3</sub>	Disks with $w = 2$ – $3.5$ mm and $\phi = 17$ mm	830	28		0.31	178
La <sub>0.4</sub> Sr <sub>0.6</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>		830	50		0.67	178
La <sub>0.2</sub> Sr <sub>0.8</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>		830	50		0.89	178
YSZ with a porous Ag electrode layer, coated with 1wt% Sr/La <sub>2</sub> O <sub>3</sub>	External current, tubular (o.d. = 20 mm and i.d. = 17 mm)	975	82	4.1	—	174
SrCe <sub>0.95</sub> Yb <sub>0.05</sub> O <sub>3</sub> with porous Ag electrodes	Disks with $w = 1.5$ mm and $\phi = 21$ mm	750	76	<1	$0.83 \times 10^{-1}$	179
La <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>0.6</sub> Fe <sub>0.4</sub> O <sub>3</sub>	Disks with $w = 1.85$ mm and $\phi = 21.8$ mm	900	70.8	12.8	13.4	176
Bi <sub>1.5</sub> Y <sub>0.5</sub> O <sub>3</sub>	Disks with $w = 1.4$ mm and $\phi = 21$ mm	950	40	16	95	180
BaGe <sub>0.8</sub> Gd <sub>0.2</sub> O <sub>3</sub>	Tubular (o.d. = 6 mm and i.d. = 4.6 mm, and $L = 30$ cm)	778	63	16.5	0.35	175
Bi <sub>1.5</sub> Y <sub>0.3</sub> Sm <sub>0.2</sub> O <sub>3</sub>	Disks with $w = 1.3$ mm and $\phi = 21.8$ mm	900	80	17	63	181
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	Disks with $w = 1.85$ mm and $\phi = 21.8$ mm	875	72	1.8	1.14	182
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub> (without catalyst)	Tubular (o.d. = 7.96 mm and i.d. = 4.56 mm, and $L = 15.94$ cm)	850	50	1.8	—	183
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub> (with La-Sr/CaO catalyst)	Tubular (o.d. = 7.96 mm and i.d. = 4.56 mm, and $L = 15.94$ cm)	850	70	15	—	183

$w$  = thickness       $\phi$  = diameter       $S$  = selectivity       $Y$  = yield

Uemiya and co-workers [186] showed that SMR can be enhanced using an alumina supported Ni catalyst contained within an 80  $\mu$  Pd on Pd/23% Ag alloy membrane coated onto a porous glass tube. At a steam/CH<sub>4</sub> = 3, they achieved enhanced conversion of CH<sub>4</sub> approaching 80% at 1 atm and 500°C vs. an equilibrium value of ~42%.

Laegsgaard and co-workers [187] used a commercial Ni/MgO SMR catalyst contained within a 100  $\mu$  Pd/Ag tubular alloy membrane. At 6 atm and 500°C, CH<sub>4</sub> conversion of 51% compared to equilibrium value of 21% was obtained.

Kusakabe and co-workers [188] studied the steam reforming of methane in a membrane reactor over Ce-Zr-O<sub>2</sub>-supported metal catalysts. At 500°C, 10 wt% Ni/Ce<sub>0.15</sub>-Zr<sub>0.85</sub>-O<sub>2</sub> support showed highest H<sub>2</sub>/CO ratio (equal to 117.1). The highest activity was obtained for the Rh/Ce<sub>0.15</sub>-Zr<sub>0.85</sub>-O<sub>2</sub> catalyst for which the methane conversion was 28.1% at 500°C.

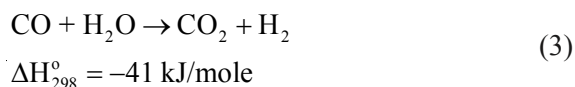
Tong and Matsumura [189] investigated steam reforming of methane over a commercial nickel catalyst in a palladium membrane on a stainless steel porous metal filter. At 0.3 MPa, 773 K and space velocity 1120 h<sup>-1</sup>, CH<sub>4</sub> conversion of about 98% was obtained.

In summary, with regard to SMR, there appears to be greater opportunity for application of membrane reactors, but significant challenges do remain. One must develop membranes with high H<sub>2</sub> flux in order to be competitive with current SMR technology, the membranes must be highly selective (preferentially permselective to H<sub>2</sub>), and the membrane device must be fabricated with durable, high temperature seals to the rest of the process unit. Attention must be paid to the possibility of carbon formation on the membrane, since commercial SMR reactors are noted for their long term reliability with a 5-year catalyst life. The high reaction temperature for SMR places a big hurdle on near term implementation of catalytic membrane reactors to SMR technology [190].

#### 4.1.4. Water–gas shift (WGS) reaction

Hydrogen as a carrier to be employed in a clean energy process has attracted a great deal of attention in the last few decades and new technologies such as polymer electrolyte fuel cells, requiring CO-free hydrogen, have promoted improvements in the H<sub>2</sub> production cycle. Light hydrocarbons represent a more realistic way to produce hydrogen and many studies on the use of catalytic membrane reactors in integrated plants for hydrogen production with low CO content have been carried out [191,192].

Currently the hydrogen produced by reforming and/or partial oxidation of light hydrocarbons, such as natural gas, contains carbon monoxide, carbon dioxide, water and a small amount of CH<sub>4</sub>. For this reason one fundamental step of the integrated membrane plant for hydrogen production is the upgrading of the streams coming from the reformer, generally consisting in water gas shift (WGS) reaction, necessary to reduce the CO content and in the meantime producing more hydrogen:



This reaction is exothermic [191,193].

A promising approach for this reaction is the use of membrane reactors, combining the reaction and H<sub>2</sub> separation through a selective membrane. Therefore, the use of a membrane reactor for the WGS reaction allows higher conversion also at higher temperature where the thermodynamic conversion is low, acting positively on the kinetics. As a consequence, the catalyst amount necessary for a given conversion can be significantly reduced. For instance, working at 280°C and 200 kPa the catalyst volume necessary to reach the 99% of the traditional reactor equilibrium conversion reduces to 1/2 of a traditional reactor using a membrane reactor with a silica membrane and to 1/3 using a Pd-alloy membrane,



at the same operating conditions [194,195]. H<sub>2</sub>-separation membranes have been developed using various materials, such as palladium and its alloys, silica and alumina, etc. Palladium–alloy membranes were successfully used for hydrogen production/separation but they have disadvantages, such as high costs, degradation of H<sub>2</sub> separation performance and, in the temperature range useful for the WGS with low temperature catalyst, the embitterment. Considerable attention has been attracted by the use of silica membrane for the WGS reaction because of the low membrane cost, the generally high permeating flux, no inhibition effect by chemical species and high thermal stability. However, generally the silica supported membrane even if shows high permeating fluxes exhibits low selectivities, therefore, the improvement of H<sub>2</sub> selectivity of this membrane type is an important issue and a balance between permeance and selectivity is essential to achieve an optimum performance. The presence of an intermediate layer between the active layer and the support is expected to improve the selectivity. One of the attractive candidates for the high permselective membrane is a silica layer formed on mesoporous  $\gamma$ -alumina film, supported on a porous stainless steel [196].

Brunetti and co-workers [196] investigated WGS reaction in a membrane reactor using a porous stainless steel supported silica membrane and a CuO/CeO<sub>2</sub> based commercial catalyst in a temperature range of 220–290°C up to 600 kPa. At 280°C and 400 kPa, they obtained a CO conversion of 95%.

#### 4.2. Membrane bio-reactors (MBRs)

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 5000 mg/L [197]. Therefore, bio-

reactor volume becomes large. On account of the difficulty of solid-liquid separation in biological wastewater treatment, MBR has been proposed and since 1960's many researches have been conducted on using MBR for water treatment [152, 198,199].

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  $\mu$ m), 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 [200–203].

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 [204]. The current MBR market has been estimated to value around US\$216 million and to rise to US\$363 million by 2010 [205].

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.

Qin and co-workers [206] used a bench scale submerged membrane bioreactor system with an

anoxic/aerobic concept and flat sheet microfiltration membranes to study the treatment and reuse of a petrochemical wastewater sample. In this system, chlorinated polyethylene with pore size 0.4  $\mu\text{m}$  was used as membrane. Typical quality of feed and MBR product water is shown in Table 16. As it can be seen from the results, the quality of MBR product met the requirement for discharge.

Kim and co-workers [207] used a dynamic state membrane bio-reactor with modified intermittent aeration (MIA) for treating sewage. In this mode of aeration, aeration period is divided into non-aeration, aeration and non-aeration (NAN). The performance of the MBR is represented in Table 17.

Tam and co-workers [208] 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 Fig. 10. 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 18.

Wisniewski [201] compares the performance of MBR system with other conventional processes (Table 19). As it can be seen, among all presented processes, a MBR system has the best performance in water treatment.

Qin and co-workers [209] investigate wastewater treatment in a membrane bioreactor pilot plant. This plant consists of anoxic reaction – aerobic reaction – membrane filtration with two submerged PVDF (polyvinylidene difluoride) hollow fiber modules. The typical analysis on raw feed and treated water are summarized in Table 20. For comparison, industrial water quality is also given in this table. As it is obvious, the treated water from this process would be suitable for industrial use.

## 5. Water and wastewater treatment

The development of new-generation mem-

Table 16  
Typical quality of feed and product [206]

Parameter	Feed	Product
COD, mg/L	720–1590	38–78
TSS, mg/L	—	<2.5
pH	6.4–10.4	7.6–8.6
Phosphate as $\text{PO}_4$ , mg/L	8.5–10.1	3.3–4.6
$\text{NH}_4\text{-N}$ , mg/L	56–132	0.10–0.95

COD: chemical oxygen demand

TSS: total suspended solid

branes that can tolerate wide pH ranges, higher temperatures and harsh chemical environments and that have improved water flux and solute rejection characteristics has resulted in many applications for the reverse osmosis (RO) process. In addition to the traditional seawater and brackish water desalination processes, reverse osmosis membranes have found applications in wastewater treatment, production of ultra pure water, water softening, food processing and many other applications.

Membrane processes have several advantages over many of the traditional separation techniques such as distillation, extraction, ion exchange and adsorption. No energy-intensive phase changes or potentially expensive solvents or adsorbents are needed for membrane separations, and simultaneous separation and concentration of both inorganic and organic compounds is possible with the RO process. Also, the RO process is inherently simple to design and operate in comparison with many traditional separation processes [17].

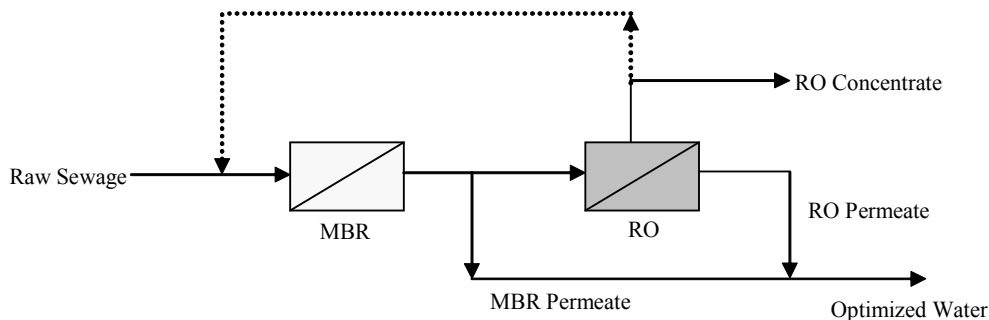
The desalination of seawater and brackish water to produce potable water is the most mature application of the RO process; this process has been used successfully over the last two decades in virtually every part of the world. Competing desalination processes include multistage flash (MSF) evaporation, vapor compression (VC), multi effect distillation (MED), solar evaporation, freezing processes and electrodialysis processes (Table 21).

Table 17  
Performance of MBR plant with MIA [207]

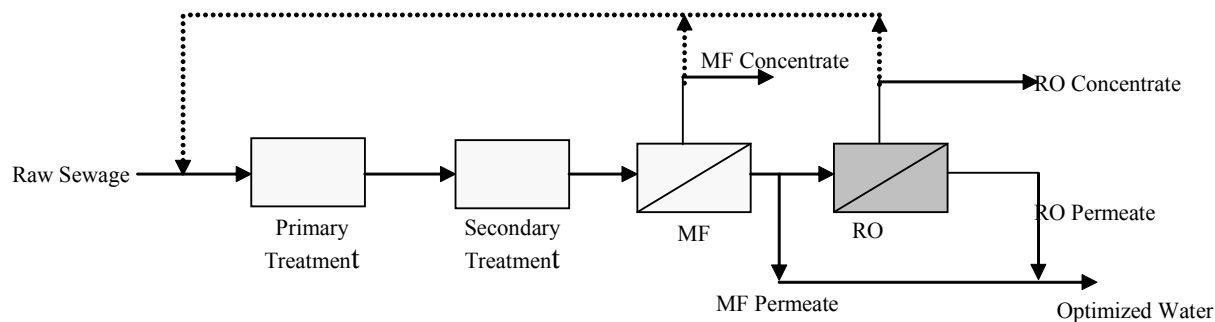
Parameter	Influent		Effluent		Removal efficiency (%)
	Range	Average	Range	Average	
BOD <sub>5</sub> , mg/L	71–186	123	0.3–3.8	2.3	98.2
COD <sub>Cr</sub> , mg/L	106–424	207	7–23	10	95.2
SS, mg/L	40–100	66	0–0.5	0.2	99.8
TN, mg/L	13–47	28	2.8–14.0	7.8	72.7
TP, mg/L	1.5–6.8	3.2	0.02–2.2	0.9	71.4
E. coli, cell/L	67×10 <sup>3</sup> –1400×10 <sup>3</sup>	528×10 <sup>3</sup>	0–80	44	99.9

BOD: biological oxygen demand  
SS: suspended solids  
TN: total nitrogen

COD: chemical oxygen demand  
TP: total phosphorous  
E. coli: *Escherichia coli*



**MBR/RO Operation**



**MF/RO Operation**

Fig. 10. An illustration of MBR/RO and MF/RO systems [208].



Table 18  
Performance of MBR/RO and MF/RO systems [208]

Parameter	MBR/RO system			MF/RO system		
	Feed	MBR effluent	RO permeate	Feed	MBR effluent	RO permeate
BOD <sub>5</sub> , mg/L	198	<2	<2	3	<2	<2
COD <sub>cr</sub> , 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 <sup>7</sup>	3.4 (44.3%)	ND	2.8×10 <sup>7</sup>	2 (19.7%)	ND
TKN, mg/L	43.0	1.6	0.1	3.1	1.5	0.4

ND: not detected

TKN: total Kjeldahl nitrogen (the sum of organic N<sub>2</sub>, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>)

Table 19  
A comparison between different treatment processes [201]

Process	Raw water			Treated water		
	TSS (kg/m <sup>3</sup> )	COD (kg/m <sup>3</sup> )	Turbidity (NTU)	TSS (kg/m <sup>3</sup> )	COD (kg/m <sup>3</sup> )	Turbidity (NTU)
Trickling bed	0.2	0.7	120	0.035	0.125	10
Activated sludge	0.2	0.7	120	0.030	0.080	5
Physico-chemical process	0.2	0.7	120	0.060	0.130	20
MBR process	0.2	0.7	120	0	0.020	<2

Turbidity: cloudiness of water caused by individual particles (NTU: nephelometric turbidity units )

Table 20  
Performance of a MBR system [209]

Parameter	Raw feed	Treated water	Industrial water quality
Ammonia-N, mg/L	26.2–38.1	2–15	5–15
COD, mg/L	87–800	30–80	50–80
Nitrate-N, mg/L	<0.01	0.3–10	5–10
pH	6.7–7.5	6.5–7.0	6.8–7.3

Many comparisons have been made between these processes, and while MSF is the major procedure of potable water, many agree that RO will account for an increasingly larger fraction of desalinated water in the future because of the ad-

vantages of the RO process. These advantages include lower energy requirements, lower capital and operating costs, low land and space requirements, reduced equipment corrosion problems, ease of construction, operation and maintenance

Table 21  
Processes for water desalination [22]

	With a phase change	Without a phase change
Evaporation	Multistage flash evaporation, vapor compression	—
Crystallization	Freezing, hydrate	—
Membranes	Membrane distillation	Reverse osmosis, electrodialysis
Others	—	Ion exchange

due to the modular nature of the process, and short construction times [22]. Use of RO in water desalination industry is now increasing and taking large fraction compared to distillation.

The MSF process accounts for the second largest installed desalting capacity in the world. The major users of MSF are Saudi Arabia, United Arab Emirates and Kuwait. The unit costs declined over time, from about 9 \$/m<sup>3</sup> in 1960 to about 0.9 \$/m<sup>3</sup> in 2000. Since MSF is mostly used for seawater desalination plants, the costs reflect the value of desalting seawater. The trend indicates that the desalting costs of seawater are expected to decrease further in the future. At present, RO has the largest share of the total installed capacity in the world. The operating cost of RO plants has been reduced thanks to two developments: (1) lower-cost, higher-flux, higher salt-rejecting membranes that can operate efficiently at lower pressures and (2) the use of pressure recovery devices. Compared to the costs of MSF, costs for RO have been much lower [210].

Saudi Arabia is an important market for desalination plants because of its large-scale desalination activity. Saudi Arabia adopts MSF, and to a less degree RO. The cost of capital is the most important determinant of desalination cost in Saudi Arabia. Table 22 lists past and recent average unit costs of producing desalinated water in Saudi Arabia for both MSF and RO plants as compared to world cost estimates [211].

Tables 23 and 24 give capacity for some of the world's largest desalination plants for seawater and brackish water respectively.

Table 22  
Unit cost of desalination in Saudi Arabia (\$/m<sup>3</sup>) [211]

Year	MSF	RO
1970–1985	1.6	0.7
1991	1.2	1.3
1995	0.6	0.8
World estimate	0.75–2.5	0.75–2.5

Reverse osmosis has also been used to treat many process streams in the petroleum industry. Because many of the separations performed in the petroleum industry involve chemicals that damage or degrade membranes, RO has been used almost exclusively to treat wastewaters. The composition of wastewaters generated by the petroleum industry is almost as diverse as the range of products produced. In the past, many of these wastewaters have been treated using biological processes (e.g. activated sludge). However, these wastewaters contain components that can inhibit the action of the organisms in the sludge, rendering the process ineffective. An alternative treatment technique, air flotation, also has limitations. Air flotation is used to remove most of the suspended or “free” oils from wastewaters, but it cannot be used to remove water-soluble low molecular weight organics. In some cases, the concentration of oils in the treated wastewater remains too high to allow discharge into the environment. As a result, other treatment options are employed, such as solvent extraction, wet oxidation, carbon adsorption, and RO.

Table 23  
Some of the large seawater reverse osmosis plants

Location	Capacity (m <sup>3</sup> /d)	Feed (mg/l TDS)	Membrane	Reference
Israel, Ashkelon	330,000	40,750	Dow Film Tec membrane	[212]
United Arab Emirates, Fujairah	170,500	38,500	SWC3 and ESPA1 Hydranautics membranes	[213]
Saudi Arabia, Al Jubail	91,000	46,500	DuPont B- 10 TWIN	[214]
Chile, El Coloso	45,360	36,500	Dow Film Tec membrane	[215]
Libya, Tajoura	10,000	36,479	Fluid Systems, TFC 2622 SS-360 and TFC 1501 PA and TFC 8600 PA	[216]
Italy, San Filippo del Mela	5184	42,300	TFC®2822 HF-370	[217]
Gaza Strip, Deir El Balah	2030	35,000	—	[218]
Italy, San Filippo del Mela	1560	42,000	TFC®8822HR-400	[217]

Table 24  
Some of the large brackish water reverse osmosis plants

Location	Capacity (m <sup>3</sup> /d)	Feed (mg/l TDS)	Membrane	Reference
Riyadh, Manfouha	63840	1350	—	[219]
Canary Island	6000	11000	Fluid Systems' TFC®8822HR	[220]
Iran, Zahedan	5760	2930	Film Tec spiral wounded Ro element	[221]

RO-based systems for the recovery of oily wastewaters are now on the market or in the pilot plant stage. However, extensive pretreatment is often required to maintain high performance because of the composition of the wastewater. Despite the need for these complicated pretreatment trains, RO is still considered a viable treatment method for oily wastewaters produced by the petroleum industry and for oily wastewaters produced by many other industries.

## 6. Summary

In the mid decades of the 20th century, industrial world understood that they should not rely solely on crude oil as an energy source; and solar energies, nuclear energies and the like could be a

better substitution with the current energy sources. Therefore, non-petroleum sources became gradually important and processes such as OCM and GTL (gas to liquid), which are based upon using natural gas in order to produce fuels, are being developed.

A decrease in petroleum sources and a great fluctuation in their prices are the principal motivations that in near future, non-petroleum sources be used for the production of petrochemical materials as the feed of petrochemical plants.

In the case of separation operations, currently available methods are easy and reliable but they are expensive, energy-intensive and environmental pollutants.

Due to the enormous potential of membranes to function as separators for mixtures of materi-

als, there has been resurgence in interest in membrane based processes. Continual efforts to develop economical and efficient membranes for various end uses have resulted in a variety of application oriented membranes.

It is clear that in near future, membranes will have an outstanding role in separation industries. Membranes work with very low energies, do not need any heating-cooling systems and do not have any environmental pollution. There is one discussable point in developing these systems and that would be their long term stability in industrial operations.

Production of polyolefins is important in petrochemical industry. An important step in the manufacture of olefins is large scale separation of olefin from the corresponding paraffin. Nowadays, this operation is carried out by distillation, which is highly energy-intensive due to cryogenic temperatures required for the process and low relative volatilities of component. Due to several advantages of membrane processes, researchers examined various membrane systems by which reasonable results were obtained in laboratory scale. Based upon large capital expense and energy cost of industrial distillation columns, it seems worthy to recommend membrane processes as a substitution with distillation columns in industrial applications. Of course, maintaining the system stability for long term operations is still questionable.

In petrochemical industry, reaction and separation play an important role in achieving desirable products. Using a membrane reactor, these two parameters can be controlled simultaneously. Dehydrogenation, oxidative coupling of methane, steam reforming of methane and water gas shift reaction are important reactions in petrochemical industry. The application of different membrane reactors to these reactions was investigated and valuable experimental results were obtained as well. In this case, it also seems attractive to consider membrane reactor in industrial applications. However, parameters such as ‘long term reliabil-

ity with catalyst life’, ‘high temperature resistance’ and ‘low coke formation’ should be considered in applying membrane reactors in industrial cases.

In case of the application of nanotechnology in the production of gas separation membranes, nano composite membranes can simultaneously improve permeability and selectivity. Producing these membranes in industrial scales, in future, refineries and petrochemical complexes will be free from huge energy-intensive distillation columns, and membrane modules can easily be replaced.

Petrochemical waste streams may contain phenolic compounds or aromatic amines. They are highly toxic and at high concentrations are inhibitory to biological treatment. Membrane aromatic recovery system (MARS) is a relatively new process for recovery of aromatic acids and bases.

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 membrane bioreactor (MBR) process.

It can be predicted that up to 2020, investments in the production of gas separation membranes will greatly increase.

## 7. General definitions

Based upon IUPAC terminology for membrane and membrane processes, there are some general definitions as below [90,91]:

*Damkohler number* — Dimensionless number equal to the characteristic time ( $l^2/D_{AM}$ ) for diffusion of complexed component across a membrane thickness,  $l$ , divided by the characteristic time ( $k_d^{-1}$ ) for the decomplexation reaction between a carrier ( $M$ ) and a complexed penetrant,  $A$ , ie  $l^2/(D_{AM}k_d)$  where  $D_{AM}$  is the effective diffusion coefficient of the complexed carrier entity in the membrane.

*Enhancement factor,  $\epsilon$*  — Ratio of the flux of a component across a carrier-containing membrane divided by the transmembrane flux of the same component across an otherwise identical membrane without carrier.

*Facilitation factor,  $F$*  — Parameter equal to the enhancement factor minus one, i.e.  $F = \epsilon - 1$

*Ideal separation factor* — Parameter defined as the ratio of the permeability coefficient of component A in a membrane to that of component B in the membrane.

*Permeability* ( $\text{cm}^3(\text{STP}) \text{cm}/\text{cm}^2 \text{s cm Hg}$ , Barrer [1 Barrer =  $10^{-10}(\text{cm}^3(\text{STP}) \text{cm})/\text{cm}^2 \text{s cmHg}$ ]) — Rate of flow of gas through a membrane of 1 cm thickness with a cross-sectional area of 1  $\text{cm}^2$  and a transmembrane differential pressure of 1 cm Hg.

*Permeance* ( $\text{cm}^3(\text{STP})/\text{cm}^2 \text{s cm Hg}$ , GPU (1 GPU =  $10^{-6} \text{cm}^3(\text{STP})/\text{cm}^2 \text{s cm Hg}$ )) — Transport flux per unit transmembrane driving force.

*Permeate* — Stream containing penetrants that leaves a membrane module.

*Retentate (raffinate)* — Stream that has been depleted of penetrants that leaves the membrane modules without passing through the membrane to the downstream.

*Separation factor* — The ability of membrane to separate gases, which is defined as  $\alpha_{ij} = (y_i/y_j)/(x_i/x_j)$ , where  $y_i, x_i$  and  $y_j, x_j$  refer to the mole fraction of components  $i$  and  $j$  in the product and feed streams respectively.

*Sweep* — Nonpermeating stream directed past the downstream membrane face to reduce downstream permeant concentration.

6FpDA	— 4,4' (hexafluoro-isopropylidene) dianiline
BPDA	— 3,3',4,4'-biphenyltetracarboxylic dianhydride
CA	— Cellulose acetate
DDBT	— Dimethyl-3,7 diaminodiphenylthiophene-5,5-dioxide
EC	— Ethylcellulose
Matrimide	— 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'aminophenyl)-1,3-trimethylindane
mPD	— 1,3-phenylenediamine
ODA	— 4,4'-oxydianiline
P4MP	— Poly (4-methylpentene-1-co- $\alpha$ -olefin)
PAAm	— Poly(acrylamide)
PDMS	— Polydimethylsiloxane
PBMA	— Poly(butyl methacrylate)
PEOx	— Poly(ethylene oxide)
PMMA	— Poly(methyl methacrylate)
POZ	— Poly(2-ethyl-2-oxazoline)
PSF	— Polysulfone
PVA	— Poly(vinyl alcohol)
PVP	— Poly(vinyl pyrrolidone)
PVMK	— Poly(vinyl methyl ketone)
Pyralin 2566	— Polyimide precursor based on 6FDA-ODA
TeMPD	— 2,3,5,6-tetramethyl-1,4-phenylenediamine
Thermid	— 6FDA based oligomer
Torlon AI-10	— Poly(amide-imide) precursor as supplied
TrMPD	— Trimethylphenylenediamine

## 8. Abbreviations

A detailed description of the abbreviated names used in Table 6 and Table 13 is given below:

1.2PB	— 1,2-polybutadiene
33'DMDB	— 3,3'-dimethyl-4,4'diaminophenyl
6FDA	— 4,4' (hexafluoroisopropylidene) diphthalic anhydride

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