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Introduction - A review of membrane reactors

Fausto Gallucci
University of Calabria

Angelo Basile
Eindhoven University of Technology

Faisal Ibney Hai
University of Wollongong, faisal@uow.edu.au

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Introduction - A review of membrane reactors

Abstract

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Introduction – A review on membrane reactors

Fausto Gallucci², Angelo Basile¹, Faisal Ibney Hai³

1. *Chemical Process Intensification, Faculty of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB, Eindhoven, The Netherlands*
2. *Institute on Membrane Technology, ITM-CNR c/o University of Calabria via P. Bucci, cubo 17/C 87030 Rende (CS, Italy)*
3. *Environmental Engineering, The University of Wollongong, Northfields Ave, NSW 2522, Australia*

Introduction

In the last decades, membrane catalysis has been studied by several research and the significant progress in this field is summarized in several review articles (Armor 1998, Lin 2001, Lu 2007, Mcleary 2006, Sanchez 2002, Saracco 1994, Shu 1991).

Considering a IUPAC definition (Koros 1996), a membrane reactor (MR) is a device for simultaneously performing a reaction (steam reforming, dry reforming, autothermal reforming, etc.) and a membrane-based separation in the same physical device. Therefore, the membrane not only plays the role of a separator, but also takes place in the reaction itself. The term Membrane Bioreactor (MBR), on the other hand, refers to the coupling of biological treatment with membrane separation in contrast to the sequential application of membrane separation downstream of classical biotreatment (Judd 2008, Visvanathan 2000). This chapter comprises a review of both MR (section 1-4) and MBR (section 5).

1. Membranes for MR

The membranes can be classified according to their nature, geometry and separation regime. In particular, they can be classified into organic, inorganic and organic/inorganic hybrids.

The choice of membrane type to be used in MRs depends on parameters such as the productivity, separation selectivity, membrane life time, mechanical and chemical integrity at the operating conditions and, particularly, the cost.

The discovery of new membrane materials was the key factor for increasing the application of the membrane in the catalysis field. The significant progress in this area is reflected in an increasing number of scientific publications, which have grown exponentially over the last few years, as recently shown by McLeary *et al.* (2006).

Generally, the membranes can be even classified into homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; they can possess a positive or negative charge as well as they can be neutral or bipolar. In all cases, a driving force as a gradient of pressure, concentration, etc., is applied in order to induce the permeation through the membrane.

Thus, the membranes can be categorized according to their nature, geometry and separation regime (Khulbe 2007).

The first classification is by their nature, which distinguishes the membranes into biological and synthetic ones, which differ completely for functionality and structure. *Biological membranes* are easy to manufacture, but present many disadvantages such as limited operating temperature (below 100 °C), limited pH range, drawbacks related to the clean-up, susceptibility to microbial attack due to their natural origin (Xia 2003).

Synthetic membranes can be subdivided into organic (polymeric) and inorganic (ceramic, metal) ones. *Polymeric membranes* commonly operate between 100 – 300 °C (Catalytica 1988), *inorganic ones* above 250 °C. Moreover, inorganic membranes show both wide tolerance to pH and high resistance to chemical degradation. Referring to the organic membranes, it can be said

that the majority of the industrial membrane processes are made from natural or synthetic polymers. Natural polymers include wool, rubber (polyisoprene) and cellulose, whereas synthetic polymers include polyamide, polystyrene and polytetrafluoroethylene (Teflon).

In the viewpoint of the morphology and/or membrane structure, the inorganic membranes can be even subdivided into porous and metallic. In particular, as indicated by IUPAC (Koros 1996) definition, *porous membranes* can be classified according to their pore diameter: microporous ($dp < 2\text{nm}$), mesoporous ($2\text{nm} < dp < 50\text{nm}$) and macroporous ($dp > 50\text{nm}$).

Metallic membranes can be categorized into supported and unsupported ones. Supported dense membranes offer many advantages unmatched by the porous ceramic membranes. In particular, many efforts were devoted to develop dense metallic layers deposited on a porous support (alumina, silica, carbon and zeolite) for separating hydrogen with a non-complete permselectivity, but lowering the costs related to the dense metallic membranes. In fact, the kind of membranes based on palladium and its alloy is used for gas separation and in MR field for producing pure H_2 (Lin 2001) and presents as main drawback the high cost.

1.1 Polymeric membranes

Basically, all polymers can be used as membrane material but, owing to a relevant difference in terms of their chemical and physical properties, only a limited number of them is practically utilized. In fact, the choice of a given polymer as a membrane material is not arbitrary, but based on specific properties, originating from structural factors. Ozdemir *et al.* (2006) gives an overview of the commercial polymers used as membranes as well as of other polymers having high potentially for application as a membrane material. However, many industrial processes involve operations at high temperatures. In this case, polymeric membranes are not useful and, therefore, inorganic ones are preferred.

1.2 Inorganic membranes

Inorganic membranes are commonly constituted by different materials as ceramic, carbon, silica, zeolite, oxides (alumina, titania, zirconia) as well as palladium, silver etc. and their alloys.

They can operate at elevated temperatures. In fact, they are stable at temperatures ranging from 300 – 800 °C and in some cases (ceramic membranes) usable over 1000 °C (Van Veen 1996).

They present also high resistance to chemical degradation. As previously said, the inorganic membranes present a high cost as main drawback.

Table 1 sketches the most important advantages and disadvantages of inorganic membranes with respect to the polymeric ones.

So, although inorganic membranes are more expensive than the polymeric ones, they possess advantage such as resistance towards solvents, well-defined stable pore structure (in the case of porous inorganic membranes), high mechanical stability and elevated resistance at high operating temperatures.

1.2.1 Metal membranes

Conventionally, dense metal membranes are used for hydrogen separation from gas mixtures and in MR area. Palladium and its alloys are the dominant materials for preparing this kind of membranes due to its high solubility and permeability of hydrogen. Unfortunately, owing to the low availability of palladium in the nature, it results to be very expensive. Recently, supported thin metallic membranes are realized by coating a thin layer of palladium (showing thickness ranging from submicron to few microns) on a ceramic support. In this case, the advantages include reduced material costs, improved resistance to mechanical strength and higher permeating flux.

Otherwise, dense membranes selectively permeable only to hydrogen based on tantalum, vanadium, nickel and titanium are considered valid and less expensive alternative with respect to the palladium and its alloy.

A problem associated with metal membranes is the surface poisoning, which can be more significant for thin metal membranes. The influence of poisons such as H₂S or CO on Pd-based membranes is a serious problem. These gases are adsorbed on the palladium surface blocking available dissociation sites for hydrogen. The effect of small amounts of H₂S may be minimized by operating at higher temperature or by using a protective layer of platinum. CO can easily desorb at operating temperatures above 300 °C (Amandusson 2000).

1.2.2 Ceramic membranes

These membranes are made from aluminium, titanium or silica oxides. They show as advantages of being chemically inert and stable at high temperatures. This stability makes ceramic microfiltration and ultrafiltration membranes particularly suitable for food, biotechnology and pharmaceutical applications in which membranes require repeated steam sterilization and chemical cleaning. Ceramic membranes have been also proposed for gas separation as well as for application in MRs.

However, some problems remain to be solved: difficulties in proper sealing of the membranes in modules operating at high temperature, extremely high sensitivity of membranes to temperature gradient leading to membrane cracking, chemical instability of some perovskite-type materials.

1.2.3 Carbon membranes

Carbon molecular sieve (CMS) membranes have been identified as very promising candidates for gas separation, both in terms of separation properties and stability. CMS are porous solids containing constricted apertures that approach the molecular dimensions of diffusing gas

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molecules. As such, molecules with only slight differences in size can be effectively separated through molecular sieving (Fuertes 1998).

CMS membranes can be obtained by pyrolysis of many thermosetting polymers such as poly(vinylidene chloride) or PVDC, poly(furfural alcohol) or PFA, cellulose triacetate, polyacrylonitrile or PAN and phenol formaldehyde and carbon membranes can be divided into two categories: supported and unsupported.

1.2.4 Zeolite membranes

Zeolites are microporous crystalline alumina-silicate with a uniform pore size. Zeolites are used as catalysts or adsorbents in a form of micron or submicron-sized crystallites embedded in millimeter-sized granules.

One of the main drawbacks related to these membranes is represented by their relatively low gas fluxes compared to other inorganic membranes. Moreover, another important problem is represented by the zeolites thermal effect. The zeolite layer can exhibit negative thermal expansion, *i.e.* in the high temperature region the zeolite layer shrinks, but the support continuously expands, resulting in thermal stress problems for the attachment of the zeolite layer to the support as well as for the connection of the individual micro-crystals within the zeolite layer (Cejka).

1.3 Membrane housing

Concerning the applications of both organic and inorganic membranes, several configurations are conventionally used for the membrane housing. Generally, a modular configuration (parallel, in series and so on) may be combined for producing the desired effect. Membrane housing provides support and protection against operating pressures. Plate-and-frame, spiral wound, tubular and

hollow fiber systems are the most common membrane housing configurations. The advantages and disadvantages of the different membrane elements are listed in Table 2.

1.4 Membrane separation regime

Mass transport through porous and dense membranes occurs with different mechanisms. In porous membranes, molecular transport occurs depending on the membrane properties. In particular, macroporous materials, such as α -alumina, provide no separating function and are mainly used to create controlled dosing of a reactant or to support a dense or mesoporous separation layer. Transport through mesoporous membranes, such as Vycor glass or γ -alumina, is governed by Knudsen diffusion. These membranes are used as composite membranes with macroporous support materials. Microporous membranes, such as carbon molecular sieves, porous silica and zeolites, offer higher separation factors due to their molecular sieving effect.

1.4.1 Porous membrane

The different transport mechanisms in porous membranes are presented below:

Poiseuille (viscous) mechanism (Figure 1) This mechanism occurs when the average pore diameter is bigger than the average free path of fluid molecules. In this case, no separation takes place (Saracco 1994). *Knudsen mechanism* (Figure 2) When the average pore diameter is similar to the average free path of fluid molecules, Knudsen mechanism takes place. In this case, the flux of the component through the membrane is calculated by means of the following equation (Saracco 1994):

$$J_i = \frac{G}{\sqrt{2 \cdot M_i \cdot R \cdot T}} \cdot \frac{\Delta p_i}{\delta} \quad (1.1)$$

Surface diffusion (Figure 3) This mechanism is achieved when one of the permeating molecules is adsorbed on the pore wall. This type of mechanism can reduce the effective pore dimensions obstructing the transfer of different molecular species (Kapoor 1989).

Capillary condensation (Figure 4) When one of the component condenses within the pores due to capillary forces, this type of mechanism takes place. Generally, the capillary condensation favours the transfer of relatively large molecules (Lee 1986). *Multi-layer diffusion* (Figure 5)

When the molecule-surface interactions are strong multi-layer diffusion occurs. This mechanism is like to an intermediate flow regime between surface diffusion and capillary condensation (Ulhorn 1992). *Molecular Sieving* (Figure 6) It takes place when pore diameters are very small, allowing the permeation of only the smaller molecules.

1.4.2 Dense metallic membranes

In dense metallic membranes, molecular transport occurs through a solution-diffusion mechanism. In particular, in a dense palladium-based membrane, hydrogen atoms interact with palladium metal. Hydrogen permeation through the membrane is a complex process with several stages:

- dissociation of molecular hydrogen at the gas/metal interface,
- adsorption of the atomic hydrogen on membrane surface;
- dissolution of atomic hydrogen into the palladium matrix;
- diffusion of atomic hydrogen toward the opposite side;
- re-combination of atomic hydrogen to form hydrogen molecules at the gas/metal interface;
- desorption of hydrogen molecules.

At a fixed temperature, the hydrogen permeation flux through a dense palladium membrane can be expressed by means of following relation (1.2):

$$J_{H_2} = Pe_{H_2} (p_{H_2,ret}^n - p_{H_2,perm}^n)/\delta \quad (1.2)$$

where: J_{H_2} is the hydrogen flux through the membrane; Pe_{H_2} the hydrogen permeability; δ the membrane thickness; $p_{H_2,ret}$ and $p_{H_2,perm}$ the hydrogen partial pressures at the retentate and permeate sides, respectively, and n (in the range 0.5–1) is the dependence factor of the hydrogen flux on the hydrogen partial pressure.

When the pressure is relatively low (Shu 1991), $n = 0.5$ and the relation (1.2) becomes Sieverts-Fick law (1.3):

$$J_{H_2,Sieverts} = Pe_{H_2} \cdot (p_{H_2,ret}^{0.5} - p_{H_2,perm}^{0.5})/\delta \quad (1.3)$$

The thickness of a dense palladium membrane is very important because it represents a compromise between two factors. On one hand, a thinner membrane offers less flow resistance and, hence, a higher permeability. On the other hand, practical fabrication technology limits the thickness of the membrane with respect to mechanical integrity and strength.

Moreover, palladium alloys are preferred over pure palladium for two reasons. Firstly, the hydrogen permeability of some palladium alloys is higher than those of pure palladium. Secondly, pure palladium can become brittle after different thermal and hydrogenation cycles. The choice of alloying other different metals to the palladium has been studied, for example, by Hwang *et al.* (1975). The authors found that the palladium alloyed show different hydrogen fluxes depending on the metal content, Figure 7.

2. Salient features of Membrane reactors

As already said, a membrane reactor combines the chemical reaction and gas separation. The significant progress in the field of MRs is reflected in the increasing number of publications as shown in Figure 8.

Many heterogeneous gas–solid catalytic processes of industrial relevance (conventionally carried out using fixed, fluidised or trickle bed reactors) involve the combination of operations at high temperatures and in chemically harsh ambient. For these two factors, inorganic membranes are favourite over polymeric materials.

A MR can show flat (Figure 9) or tubular geometry (Figure 10). In tubular MR, the density of packed bed could be improved using multichannel tubular monoliths and depositing the catalyst inside the pores.

Generally, the MRs can be also sub-divided as reported below (and in Figure 10):

- catalytic membrane reactors (CMR);
- packed bed membrane reactors (PBMR);
- catalytic non-permselective membrane reactors (CNMR),
- non-permselective membrane reactors (NMR);
- reactant-selective packed bed reactors (RSPBR).

2.1 Applications of membrane reactors

Membrane reactors are mainly used to carry out the reactions limited by the equilibrium conversion such as water gas shift and so on. In fact, in a MR the separation capability of a membrane is utilized to improve the performance of a catalytic system. Usually, there are two main generic approaches: selective product separation (Extractor) and selective reactant addition (Distributor), as shown in Figure 11 (Julbe 2001a). The first MR type facilitates the in-situ removal of one of the products (Figure 11.a). For example, for steam reforming reactions, H₂

yield and CO₂ product selectivity in TRs are limited by Thermodynamics. By selective removal of H₂ from the reaction side, the thermodynamic equilibrium restrictions can be overcome. Due to the shift effect, both high H₂ yields and high CO₂ selectivities can be achieved. Moreover, this effect allows operation at milder reaction conditions in terms of temperature and pressure (Zaman 1994).

The second kind of MR uses the membrane to control the contact within reactants (Figure 11.b). Both a permselective and a non-permselective membranes can be used to feed distributively one of the reactants. For partial oxidation reactions in TRs, O₂ rich feed results in low product selectivity and high reactant conversions. On the contrary, low oxygen content feed results in high product selectivity but lower conversions. Using a membrane for distributive feeding of O₂ along the axial coordinate of the catalytic bed, both high reactant conversions and high product selectivities can be combined (Bredesen 2004, Coronas 1999, Julbe 2001a, Saracco 1999). An additional advantage of this approach is that the reactant (hydrocarbon) and O₂ feeds are not premixed and, hence, the possibility of realizing mixtures as well as the flame back firing into the feed lines are greatly reduced. Moreover, the feed distribution can represent a promising approach for fast reactions.

2.2 Advantages of the membrane reactors

With respect to TRs, a MR permits the improvement of the performances in terms of reaction conversion, products selectivity, and so on. In fact, by means of the so-called “shift effect”, the thermodynamic equilibrium restrictions can be overcome. At least, MRs behaviour could be the same of a TR working at the same MRs operating conditions.

Keizer *et al.* (1994) studied the performances of several MRs using different kind of membranes.

As reported in Figure 12, they represent the dependence of the cyclohexane conversion as a

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function of the parameter H , defined as permeation to reaction ratio and considering the Damköhler number (Da) equal to 1. The line with $H = 0$ represents a TR, while other lines correspond to a different type of MRs. In particular, lines 1-2 refer to MRs governed by Knudsen transport mechanisms; lines 3-4 refer to microporous MRs and lines 5-6 refer to dense ones. Two regions can be distinguished. The first one corresponds to low permeation to reaction rate ratios. In this region, microporous MRs show the same behaviors of dense and mesoporous ones. However, the performance of each MR types in terms of conversion is better than the TRs ones. At higher H -values, the difference in the MRs properties are visible. MRs with a finite separation factor show an optimum permeability/reaction rate region. Above optimum the reactant loss due to permeation induces a detrimental effect on the conversion. The higher the separation the higher the conversion in this optimum region. MRs with infinite separation factors for hydrogen do not show this conversion drawback since no loss of reactants occurs. Thus, they maintain the conversion at a high value.

As shown, this kind of membranes represents an important issue concerning the MR performances in terms of conversion, hydrogen selectivity, etc.

Thus, the main advantage of using MRs is represented by the combination of reaction and hydrogen separation, leading to a reduction of capital cost and better reactor performances. Moreover, they allow also controlling additions of reactants and coupling of reactions (Saracco 1994).

3. Hydrogen production by membrane reactors

The world economy is mainly based on the exploitation of fossil fuels (oil, coal and methane) (Moriarty 2007), according to data provided by International Energy Agency reported in Figure 13. In particular, the primary energy source is oil, but owing to the decrease of its reserves and to

the increase of the environmental pollution due to emissions of CO₂ and other greenhouse gases (in the world, more than 75.0% of CO₂ emissions comes from burning of fossil fuels and, in the last 70 years, more than 30.0% of CO₂ increment as volume percentage was registered in the atmosphere (Marbà 2007)), it is strongly necessary to develop new technologies as well as to exploit renewable materials as alternative to the derived fossil fuels.

For example, fuel cells have been identified as one of the most promising technologies for the future clean energy industry (Stambouli 2002). They can be applied to large-scale stationary systems for distributed power generation as well as for small-scale portable power supplying devices for micro-electronic equipment and auxiliary power units in vehicles (Wee 2007). Compared to other types of fuel cells, PEMFCs generate more power for a given volume or weight of fuel cell. This high-power density characteristic makes them compact and lightweight. PEMFCs are fed by pure hydrogen and only few ppm of CO (<10) may be tolerated by the anodic Pt catalysts. For this reason, it is strictly necessary to use a pure or at least CO-free hydrogen stream for feeding a PEM fuel cell.

Industrially, hydrogen is produced in fixed bed reactors by means of reforming reactions of fossil fuels such as natural gas, gasoline, etc. Nevertheless, as previously mentioned, in order to solve the problems related to the environmental pollution, it is necessary the exploitation of renewable materials. Therefore, hydrogen could be produced using “clean” fuels (Goltsov 2001).

The steam reforming reaction is conventionally carried out in fixed bed reactors and produces a stream containing hydrogen with other byproduct gases like mainly CO, CH₄ and CO₂. Therefore, in the viewpoint of feeding a PEMFC, hydrogen needs to be purified by means of the following processes: water gas shift (WGS) reaction, pressure swing adsorption and/or Pd membrane separation, etc. Otherwise, it could be economically more advantageous to use a

hydrogen perm-selective MR, able to both carry out the reaction and remove pure hydrogen in the same device (Basile 2008a, Cheng 2002, Damle 2009, Matsumura 2008, Tosti 2000, Valenti 2008). In particular, with respect to the traditional reactors (TRs), MRs are able:

- to combine chemical reaction and hydrogen separation in only one system reducing the capital costs;
- to conversion enhancement of equilibrium limited reactions;
- to achieve higher conversions than TRs, operating at the same MR conditions, or the same conversion, but operating at milder conditions;
- to improve yield and selectivity.

Moreover, as previously said, the most useful membranes offering a complete hydrogen perm-selectivity are the dense palladium-based ones (Lu 2007). The transport mechanism related to the hydrogen permeation through a dense Pd-based membrane is the solution/diffusion (Ward 1999). Generally, when a dense Pd membrane is exposed to a hydrogen stream at low temperatures (< 300 °C), the embrittlement phenomenon takes place owing to the various typologies of expansion of the reticular constants in the Pd-H systems. A possible solution is represented by alloying palladium with elements, such as silver or copper, in order to obtain Pd-H phases with increased reticular step and able of anticipating the reticular expansion from hydrogen (Hou 2003).

Since 1960s, hydrogen production by MRs has been mainly studied using dense Pd-based membranes and microporous silica membranes. Pd membranes for H₂ production overcome all the other candidate materials due to of the very high solubility of H₂ in pure Pd (Figure 14) and for their infinite perm-selectivity to H₂.

In particular, Pd adsorbs 600 times its volume of H₂ at room temperature (Julbe 2001b). For this characteristics, Pd or Pd alloys on metallic or ceramic supports have been widely studied (Amandusson 2001, Dittmeyer 2001, Kikuchi 2000, Li 1993, , Paturzo 2002, Roa 2003, Shu 1996, Tong 2005a, Tosti 2003 Uemiya 1991, Wang 2004, Zhang 2006).

Therefore, as stated in the first part of this paragraph, it is very interesting to investigate the production of hydrogen by means reforming reaction of renewable sources, using the innovations connected to the MRs. However, in the following a small overview is presented on the hydrogen production based on the classic processes such as methane steam reforming, methane dry reforming and partial oxidation of methane as well as water gas shift reaction coupled with the use of membrane reactors.

3.1.1 Methane steam reforming

Conventionally, hydrogen is produced by exploiting methane as a derived fossil-fuel in reforming reactions. Currently, 80.0–85.0% of the world wide hydrogen supplying is produced by methane steam reforming (SRM) (3.1.1.1) reaction in fixed bed reactors (Simpson 2007).

Alternatively, methane could be renewably obtained via biogas generated by the fermentation of organic matter including manure, wastewater sludge, municipal solid waste (including landfills) or any other biodegradable feedstock, under anaerobic conditions. The composition of biogas varies depending on the origin of the anaerobic digestion process. Advanced waste treatment technologies can produce biogas with 55.0 – 75.0% of CH₄ using in situ purification techniques (Richards 1994).

However, most part of the specialized literature on SRM area is devoted to study the optimal reaction conditions and the most adequate catalyst usable during the reaction in TRs.

In the last decades, the alternative technology of the membrane reactors has been applied to SRM reaction in order to produce hydrogen with the advantages previously reported in this work. In particular, recent reviews regarding the state-of the-art on the hydrogen production via SRM reaction performed by MRs have been published (Ritter 2007, Barelli 2008). Moreover, different scientific papers deal on various MRs (based mainly on dense palladium and its alloy membranes) for hydrogen production by SRM reaction (Chen 2008, Gallucci 2008c, Haag 2007, Tong 2005b, Tsuru 2006a).

3.1.2 Dry reforming of methane

Another approach for hydrogen production in MRs is the dry reforming of methane (3.1.2.1):

In particular, methane dry reforming reaction could reduce the amount of greenhouse gases present in the atmosphere. An important limitation for making the methane dry reforming a commercially viable reaction using TRs is due to Thermodynamics, which limits the conversion. Nevertheless, in a MR, methane (and carbon dioxide) conversion can be increased though the reaction products (or preferentially only hydrogen) are selectively removed from the reaction side.

Gallucci *et al.* (2008) performed the dry reforming reaction in both TR and MR with the aim of consuming carbon dioxide and producing hydrogen. Moreover, by using the dense Pd membrane reactor, the carbon deposition on the catalyst is drastically reduced and a CO-free hydrogen stream is produced. At 450 °C, the maximum CO₂ conversion obtained in the MR was around 20.0% versus 14.0% achieved in the TR.

Haag *et al.* (2007) studied the methane dry reforming reaction in a composite MR, where the membrane was constituted of a thin, catalytically inactive nickel layer, deposited by electroless plating on asymmetric porous alumina with acceptable hydrogen perm-selectivity at high temperature. Ferreira *et al.* (2002) analyzed the applicability of mesoporous ceramic filters in a MR to carry out the dry reforming of methane with carbon dioxide. **3.1.3 Partial oxidation of methane**

Both steam reforming and dry reforming of methane are endothermic reactions. On the contrary, the partial oxidation of methane (POM) (3.1.3.1) is an exothermic reaction, in which the main drawback in TRs is represented by the Thermodynamics. For example, the pressure increase gives a decrease in equilibrium methane conversions

Therefore, a MR allows these thermodynamic limitations to be overcome, reaching a high methane conversion at low temperature with respect to a TR.

By using a dense Pd-based MR with respect to a TR exercised at same conditions, Basile *et al.* (2001a, 2001b) stated that:

- the methane conversion is remarkably higher in MRs than in the TRs, at a fixed temperature.
- the Pd-based MR shows the highest methane conversion (96.0% at 550 °C and 1.2 bar).
- the MR methane conversions exceed the thermodynamic equilibrium conversion.

Yin *et al.* (2008) used a tubular MR for correlating air separation with catalytic POM. The MR consisted of three annular layers: a porous and thin cathodic layer, a dense and thin mixed conducting layer and a porous, thick anodic layer. At 850 °C, high methane conversion (>90.0%), CO selectivity (>90.0%) and hydrogen selectivity (>80.0%) were obtained as best result.

Cheng *et al.* (2009) using a MR equipped with a Pd-based membrane for carrying out the POM reaction, obtained as best result 97.0% of hydrogen purity, 85.0% of methane conversion and 98.0% of oxygen conversion.

3.2 Water gas shift reaction performed in membrane reactors

Conventionally, the WGS reaction is limited in terms of thermodynamic constraints. As a consequence, the interest of scientists seems quite justified in searching for alternatives to TRs (Mendes 2009). In different scientific works, the WGS reaction carried out in MRs was analyzed while paying attention to the influence of different parameters such as reaction temperature and pressure as well as sweep-gas flow rate and feed molar ratio. In particular, two opposite effects on the MR system occur when increasing the reaction temperature. A temperature increase induces a positive effect in terms of higher hydrogen permeability through the membrane, enhancing the hydrogen permeating flux from the reaction to the permeate side, resulting in a shift towards the reaction products with a consequent increase of CO conversion. On the contrary, since the WGS reaction is exothermic, at higher temperature a detrimental effect on the equilibrium CO conversion is produced.

3.3 Outlines on reforming reactions of renewable sources in membrane reactors

Clean and renewable sources can be produced for example by biomass, which mainly presents the following advantages:

- it is a renewable source;
- it is widely available;
- it can be processed and converted into liquid fuel (bio-fuel).

Moreover, using biomass energy, the carbon dioxide atmospheric levels are not increased because of the cycles of re-growth for plants and trees; the use of biomass can also decrease the amount of methane, emitted from the decay of organic matter;

An outline of production methods of the biosources is shown in Figure 15, whereas a list of the main biofuels is reported below:

1. bioethanol: ethanol produced from biomass and/or the biodegradable fraction of waste;
2. biomethanol: methanol produced from biomass;
3. biodiesel: a methyl-ester produced from vegetable or animal oil;
4. bioglycerol: glycerol produced as by-product of biodiesel production;
5. biogas: a fuel gas produced from biomass and/or the biodegradable waste that can be treated in a purification plant in order to achieve a quality similar to the natural gas.

The biosources shown in Figure 15 can be converted in hydrogen via reforming reactions (autothermal reforming, steam reforming, partial oxidative steam reforming). Therefore, in the following sections, a summary of scientific studies made since 2000s on steam reforming reactions of biosources performed in MRs is given. In particular, a small overview on the membrane type, the operative conditions, and performances in terms of hydrogen recovery and reaction conversion obtained performing the steam reforming reaction of different bio-sources in MRs is reported in Table 3.

The steam reforming is an endothermic reaction, which is generally carried out in TRs at high temperatures ($> 600\text{ }^{\circ}\text{C}$) and pressures ($> 10\text{ bar}$). Vice versa, as illustrated in Table 3, the MRs reaction temperatures commonly range between 250 and 600 $^{\circ}\text{C}$ and the pressure varies between 1 and 8 bar. Moreover, Table 3 illustrates also the MR ability to obtain almost complete conversion and a pure or, at least, CO-free hydrogen stream to be fed for example to a PEMFC.

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4 Other examples of membrane reactors

Ultra-pure hydrogen production is surely the field in which membrane reactors are being applied, because of the possibility of combining the separation and reaction in one compact reactor, resulting in both higher conversion than traditional systems and pure hydrogen production (if dense hydrogen selective membranes are used). However, membrane reactors can be used in different other applications. In this second part of the review, the recent developments in the application of membrane reactors for different reaction systems, including membrane bio-reactors will be discussed.

4.1 Zeolite membrane reactors

Among the different inorganic membrane reactors, zeolite membrane reactors gained increasing interest during the last twenty years, as demonstrated by the growing number of scientific publications and patents presented in literature (some of them discussed below).

Zeolites present a crystalline and ordered structure along with a narrow pore distribution. Zeolites are hydrated alumino-silicates, with an open crystalline structure constituted by tetrahedral SiO_4 and AlO_4^- units linked by oxygen atoms. They are structurally unique since they have cavities or pores with molecular dimension as a part of their crystalline structure as indicated by Meier (1986) and Weitkamp (2000). Around 50 zeolites have been found in nature and more than 1500 types of zeolite have been synthesised. The Structure Commission of the International Zeolite Association (IZA) is in charge to approve zeolite structures, which are classified using a three-letter code, included in the “Atlas of Zeolite Structure Types”. When a zeolite is arranged as a layer and it performs as a diffusion barrier we have a zeolite membrane. The quality and then the mass transport characteristics of the zeolite membrane mainly depend

on the zeolite type and synthesis, presence of a support and obviously the involved specie along with the operating conditions.

In Table 4 the main investigators on zeolite membrane reactors are reported:

Zeolite based membrane reactors have been used for different applications such as xylene isomerization (Deshayes 2006, Tarditi 2006 and Zhang 2009), for ethanol esterification (de la Iglesia 2007), for hydrolysis of olive oil (Shukla 2004) and for methanol production (Gallucci 2004) and different others.

In particular, Tarditi *et al* (2006) synthesis a membrane made of ZSM-5 films supported on porous SS tubes to be used for separation of xylene isomers. This separation is quite important for refinery industries. In fact, the most valuable *p*-xylene should be separated from the other isomers. Generally the isomers are separated by distillation of *m*-xylene and successive crystallization of *o*-xylene, a quite energy intensive separation route. The use of the MFI-zeolite membranes for xylene separation appears as a good alternative to the conventional route. Their results indicate that ZSM-5 membranes can be used for increasing the *p*-xylene yield. Based on the permeation characteristic found for ZSM-5 membrane, Deshayes *et al.* (2006) formulated a model for xylene isomerization in the membrane reactor. With optimized kinetics, an industrial scale reactor was simulated by taking into consideration practical restrictions on the pressure drop and on the effective diameters of the membrane tubes which were kept within physical and constructive feasibility. Within these boundaries, the authors were able to optimize their reactor confirming that a ZSM-5 membrane reactor can give 12% increase in *p*-xylene production with respect a conventional reactor. Recently, Zhang *et al.* (2009), performed an extensive study on the effects of operating conditions and membrane stability. The use of zeolite membrane reactors (mordenite and zeolite A membranes) was studied by de la Iglesia *et al.* (2007) for the

esterification of ethanol to ethyl acetate with simultaneous water removal. Tubular membrane reactor configuration has been used where catalyst was packed inside the membrane tubes. Both membranes used were able to shift the equilibrium reaction due to product removal during the reaction. The possibility of removing water and methanol via a zeolite membrane during methanol synthesis was studied by Gallucci *et al.* (2004). A zeolite A membrane was used in a packed bed membrane reactor where a commercial catalyst was used for carbon dioxide hydrogenation. The experimental results show a good performance of the membrane reactor with respect to the traditional reactor: at the same experimental conditions, CO₂ conversion for the membrane reactor was higher than that related to the traditional reactor. Zeolite membranes can be also used in Fisher-Tropsch reaction system for water removal as indicated a.o. by Rohde *et al.* (2008).

4.2 Fluidized bed membrane reactor

Fluidized bed membrane reactors are being studied for different applications and by different research groups as indicated in the following Table 5.

The integration of membranes (dense or porous, generally non catalytic) inside a fluidized bed reactor, allows to combine the benefits of both separation through membrane and benefits derived from fluidization regime. It is well known that packed bed membrane reactors suffer from the same disadvantages of packed bed reactors; that is to say: Relatively high pressure drop, possible mass transfer limitations owing to the relatively large particle size to be used, radial temperature and concentration profiles, difficulties in reaction heat removal or heat supply, low specific membrane surface area per reactor volume.

On the other hand, as summarized in the review presented by Deshmukh (2007a), the main advantages of the fluidized bed membrane reactors are:

- Negligible pressure drop; no internal mass and heat transfer limitations because of the small particle sizes that can be employed.
- Isothermal operation.
- Flexibility in membrane and heat transfer surface area and arrangement of the membrane bundles.
- Improved fluidization behavior as a result of:
 - ✓ Compartmentalization, i.e. reduced axial gas back-mixing.
 - ✓ Reduced average bubble size due to enhanced bubble breakage, resulting in improved bubble to emulsion mass transfer.

Some disadvantages are of course foreseen such as:

- Difficulties in reactor construction and membrane sealing at the wall.
- Erosion of reactor internals and catalyst attrition.

The last disadvantage can be really critical if high selective thin layer membrane is used inside the fluidized bed. Any erosion on the membrane surface can result in a decreased permselectivity and a decrease in overall membrane reactor performance. For this reason, membranes to be used in fluidized membrane reactors should be protected by erosion, perhaps by using a porous media between the membrane layer and the fluidized bed. Fluidized bed membrane reactors for pure hydrogen production are studied by different research groups (example Rahimpour 2009a, Gallucci 2008a,b, Mahecha-Botero 2008 and Abashar 2007). In this case, as discussed in the first part of the review, Pd-based membranes are inserted in fluidized bed reactors where reforming of hydrocarbons takes place. On the other hand, fluidized bed membrane reactors have also been proposed for different applications. In particular, Deshmukh *et al.* (2005a,b) developed a membrane-assisted fluidized bed reactor for the partial oxidation of

methanol. At first the authors performed cold experiments in order to study gas phase back-mixing (via tracer injection technique) and bubble-to-emulsion phase mass transfer (using ultrasound experiments). A scheme of the tracer injection set-up is reported in the following figure 16. With this technique, the authors demonstrated that effective compartmentalization of the fluidized bed is realized especially in the case of gas permeation through horizontal membranes inserted in the fluidized bed. Based on this study, the same authors (Deshmukh 2005b) built a small scale experimental set-up for partial oxidation of methanol inside a fluidized bed membrane reactor. The effects of different operating conditions on the methanol conversion to formaldehyde have been evaluated and the results compared with a phenomenological model for the fluidized bed membrane reactor.

The experimental set-up is shown in the following Figure 17.

The authors demonstrated that distributive feeding of oxygen in a fluidized bed membrane reactor produces an increased overall formaldehyde yield and throughput without pronounced conversion of formaldehyde to carbon monoxide.

Prof. Rahimpour's group proposed the application of fluidized bed membrane reactors for different reaction systems. In particular, an example of fluidized bed applied to Fisher-Tropsch reaction system can be found in Rahimpour (2009b). In this work Pd-based membranes are inserted in a fluidized bed in a two reactors plant as indicated in Figure 18. The addition of hydrogen through the Pd-based membranes inside the fluidized bed keeps the H_2/CO ration to an optimal value (or close to it), resulting in a better overall performance. On the other hand, the use of fluidized bed membrane reactors also solves some drawbacks of packed-bed reactors already discussed such as high pressure drop, heat transfer problem and internal mass transfer limitations.

4.3 Perovskite membrane reactors

The first report of oxygen permeation through perovskite based materials was probably Teraoka and co-workers (1985), who studied the oxygen flux through 10 mm disks shaped perovskite based material. After more than 20 years from this interesting report, no industrial applications of perovskite membrane exist yet. This is mainly due to difficulties in membrane/module sealing at high temperature (high temperature needed for achieving a reasonable oxygen flux), to problems in membrane stability, and to lack of membrane modules with high surface area per volume. The last problem is addressed by using hollow fibre membrane reactor configurations as discussed in the following section. In this section, some examples of perovskite membranes used in membrane reactors are presented. The main investigators on perovskite membrane reactors are reported in Table 6.

A recent example of perovskite membrane reactor has been presented by Sun and co-workers (2009) in order to oxidize the ammonia to NO (for nitric acid production). Actually, 80% of the ammonia is used for fertilizers production, and a big part is first converted to nitric acid through a high temperature oxidation on platinum-rhodium alloy catalyst. This reaction is well known since years and also well optimized in terms of catalyst. However, still some technological problems have to be faced. In particular, this operation is quite cost intensive also due to catalyst loss as oxides. This problem is being studied by exploring some other catalysts such as Cr_2O_3 or Co_3O_4 . However, N_2O emissions from these plants are the greatest among chemical industries, which means that costly N_2O capture systems are required.

Sun *et al.* (2009) show the application of a perovskite membrane reactor to carry out the separation of oxygen and the reaction in one unit.

The scheme of the reactor is depicted in Figure 19.

Air is fed from one side of the membrane, and oxygen is dissociated on the membrane surface into O_2^- . The ion O_2^- diffuses through the membrane due to the difference in oxygen partial pressure between the two membrane surfaces. On the other membrane surface, ammonia is fed and selectively reacts with the oxygen diffusing through the membrane to form NO.

The membrane proposed and studied by Sun is a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite in form of discs with a thickness of 1.4 mm. The membrane is housed in a reactor consisting in two quartz tubes. Most of the articles related to perovskite membranes in membrane reactor deals with reactions involving natural gas or hydrocarbons. In the following, examples of membrane reactors for oxidative coupling of methane (Olivier *et al.* 2009), partial oxidation of methane (Li *et al.* 2009) and methane reforming (Yeremchenco *et al.* 2008) will be discussed.

Another system where perovskites can be used as membrane reactors is the methane partial oxidation, an interesting route for producing syngas from methane. The reaction has already been discussed as a promising route for hydrogen production (in dense Pd based membrane reactors) in section 3.1.3 and it is as follows:

When focusing on syngas production the reaction leads to a syngas with a ratio $H_2/CO = 2$, which makes the reaction system more interesting than the typical methane steam reforming. In fact, according to Keinert (2006) the syngas ratio = 2 is the optimum for different post-processing system while the methane steam reforming gives a syngas ratio = 3.

The problem of POM is that pure oxygen is needed in order to produce syngas, resulting in quite expensive air separation units and makes the operation quite risky because the direct contact between methane and pure oxygen at high temperature may result in explosions. Air can not be

used because nitrogen would contaminate the syngas and would also react to produce NO_x. For this reason, oxygen permeating membranes are quite attractive for this reaction system too.

Li and co-workers (2009) studied POM in a BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-δ} membrane reactor by using a LiLaNi-based catalyst. Another interesting work has been presented by Yaremchenko *et al.* (2008), who studied the effect of perovskite-like tubular membrane for reforming of methane. The aim is to demonstrate the possibility to carry out the POM reaction with oxygen addition through tubular membranes (thus with higher area/volume than the flat membrane). The promising results will drive the research towards an optimization of the membrane material as well as a better reactor design (such as hollow fibre membrane reactor) in order to optimize the oxygen flux inside the reactor.

4.4 Hollow fiber membrane reactors

An interesting membrane reactor configuration is the hollow fiber membrane reactor, which allows achieving much higher membrane area/reactor volume than the other membrane reactors configurations. The membrane area available is an important parameter for all the membrane systems. However, it becomes really important when membranes with low permeation fluxes are used. A good example is the use of polymeric membranes in gas separation. It is quite evident that the driving force for industrial exploiting of polymeric membrane systems, for example in natural gas treatment as well as dialysis applications, was the availability of hollow fiber membranes and membrane modules.

Following this example, many other membrane applications are looking for hollow fiber availability. For example, in case of perovskite membranes the membrane flux is generally quite low and the hollow fiber configuration is quite interesting. A pioneer on ceramic hollow fiber

membrane is surely Prof. Li, who contributes to this book with a chapter on hollow fiber membrane preparation. The main investigators of hollow fibre membrane reactors are summarized in the following Table 7. In the following some examples of hollow fibre perovskite membrane applications will be discussed. So far, laboratory studies on hollow fiber ceramic membrane applications use a single ceramic membrane in a configuration tube in tube or at best few hollow fibers in tubes in shell configuration. The typical tube in tube configuration is reported in Figure 20.

The applications of hollow fiber membrane reactors are in principle the same applications in which distributed oxygen feeding can be beneficial for the reaction system. A good example, often studied is the oxidative coupling of methane (OCM). This reaction system is known to be the direct route for transforming methane into C₂ products. This route is surely more economical interesting than the indirect route in which methane is first converted into syngas and then the Fisher-Tropsch process is used to convert syngas into higher hydrocarbons. OCM has been then studied by using dense ceramic membranes, and C₂ selectivity up to 95% has been obtained. However, due to the low oxygen flux and to the low membrane area per volume the total yield was not higher than 10%.

To overcome this drawback, a hollow fiber membrane reactor has been proposed by Tan and Li (2006, 2007). They prepared a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\text{R}}$ (LSCF) hollow-fiber membrane by phase inversion/sintering technique. For the details of the techniques please see the following chapters. A tubes-in-shell configuration (with 5 hollow fibers in a ceramic shell) has been used for this research. To reduce the stresses on the membranes due to the difference in thermal expansion between membranes and shell material, the authors used some rubber tubes at the ends of the membrane. Long membranes were used so that just the central part of the reactor was used in a

furnace, while the extremities were relatively cold. This is a good practice in order to avoid high temperature sealing problems. The OCM reaction was carried out in this membrane reactor, and the results suggest that C₂ yield depends on both reaction temperature and oxygen flux through membranes. Promising 15.3% C₂ yield, even though with low selectivity 44% ca, suggests that the development of OCM in perovskite hollow fiber membrane reactors is an interesting field to be explored.

Hollow fibre membrane reactors have also been studied for different reaction system. Kleinert and co-workers (2006) applied this kind of reactor to partial oxidation of methane.

As already discussed above, the problem of POM is that pure oxygen is needed in order to produce syngas, resulting in quite expensive air separation units. By using perovskite-like hollow fibre membrane reactor, a higher membrane area for the air separation is available.

The perovskite membranes used by Klainert *et al.* were produced from Ba(Co,Fe,Zr)O_{3-d} (BCFZ) powder via phase inversion spinning technique. A tube in tube configuration has been used while the catalyst was packed in the shell side of the reactor.

In their paper the authors show that the membrane was able to give quite interesting results with a methane conversion of 82% and a CO selectivity of 83%. Moreover the membrane was quite stable under the reactive conditions investigated. A comparison between the performance of perovskites in hollow fiber configuration and disk geometry as been carried out by Caro and co-workers (2006). The work is mainly based on structural study and oxygen permeation. A quite stable syngas production over 120 hr of stream has been obtained, with a 80% methane conversion and 82.5% CO selectivity, confirming the possibility of carrying out the POM reaction in hollow fibre membrane reactors.

A perovskite hollow fibre membrane reactor has been applied by Wang and co-workers (2006) for the oxidative dehydrogenation of ethane to ethylene. The direct oxidation of ethane to ethylene is an alternative route to the typical thermal steam cracking routes. However, as already discussed for OCM, the co-feeding of ethane and oxygen in a fixed bed reactor is not an option, being the deep oxidation to CO_2 a thermodynamically favored reaction.

4.5 Catalytic membrane reactors

A direct survey of the main investigators on catalytic membrane reactors is quite complicated because various authors erroneously call catalytic membrane reactor a reactor in which a catalyst is somehow packed inside the reactor. Indeed, this kind of reactor should be called packed bed membrane reactor. A catalytic membrane reactor is a special reactor where the membrane acts as separation layer and as catalyst as well. The membrane can be either self-catalytic (Dong 2008), or can be made catalytic by coating the surface of a dense membrane (Bathia 2009), or by depositing the catalyst material inside the pores of the membrane (Fritsch 2006), or by casting a solution containing the polymeric material and the catalytic material (de Souza Figueiredo 2008). Both experimental and theoretical studies have been presented on catalytic membrane reactors. A very active group in modeling polymeric catalytic membrane reactors is the group of Mendes who modeled different reaction systems in polymeric CMR with quite detailed models (see for example Mendes 2006).

Concerning the experimental works, both polymeric and inorganic catalytic membrane reactors have been used. Fritsch (2006) produced porous polymeric membranes with high fluxes with the casting machine available at GKSS (Germany). The authors followed two different routes for producing the catalytic membranes as previously indicated. Both a catalyst containing casting solution and the pore filling catalyst material have been used.

The membranes were used for the hydrogenation of sunflower oils to edible oils. The approach proposed is quite interesting since with the catalytic membrane with high fluxes the authors are able to both overcome the problem of catalyst separation from the edible oil (catalyst normally used are either expensive or toxic) and the problem related to high pressure drops induced by high viscous oils.

Bobrov and co-workers (2005) produced a catalytic membrane by depositing a catalytic layer on gas separation inorganic membrane by using the chemical vapor deposition technique. This is a quite standard procedure to produce catalytic membranes as indicated in the following chapters. The membrane produced was used for propane dehydrogenation demonstrating that probably the catalytic membranes are much more suitable for this reaction than the dense selective hydrogen permeating membranes (more difficult to produce and less stable).

4.6 Photo-catalytic membrane reactors

An interesting new system to be taken into account is the photocatalytic membrane reactor system where the photo-catalysis is somehow improved by membrane separation. The field is studied by various scientists and a list of the main investigators is reported in the following Table 8.

The photocatalytic membrane reactor can be built in two different ways. What we strictly would call a photocatalytic membrane reactor is a reactor in which the membrane is placed in contact with the reactants and on which the light is irradiated via an internal or external light source. A typical scheme can be for example the one reported in Figure 21. Similar schemes are used by Choo (2008), Huang (2007), Chin (2007) and Tsuru (2006b). A second way to work with photocatalytic membrane reactor is to separate the reaction system and the membrane separation

system (ultrafiltration, or other) in two different steps (Figure 22). This scheme has been used for example by Mozia (2008, 2009), Molinari (2009) and Azrague (2005).

The membrane often serves as separator of the suspended photo-catalyst particles from the treated media (Huang 2007). In other cases the photo-catalyst can be impregnated into the membrane media which also acts as support or the membrane itself can be photocatalytic (Tsuru 2006b). Moreover, the membrane can act as separator of the reaction products (Molinari 2009). Typical applications of photocatalytic membrane reactors are the photo-degradation of water pollutants (Mozia 2009), Photo-reaction to obtain more valuable products (Molinari 2009) and photo-oxidation of pollutant vapor compounds (Tsuru 2006b).

Where the membrane is used as external separation system, the problem reduces to a study of membrane filtration. In this case, often commercial membrane filtration system can be easily used. Different is the case in which a membrane is photocatalytic or it is supporting the catalyst. In this case, as indicated by Tsuru (2006b) the membrane needs to be prepared with a tailored amount of catalyst, with particular attention to the membrane pore size distribution and membrane photocatalytic activity towards the reaction of interest.

5. Membrane bioreactor (MBR)

Membrane separation in MBR combines clarification and filtration of a conventional activated sludge (CAS) process into a simplified, single step process. Membranes are seldom used by themselves to filter untreated wastewater, since fouling prevents the establishment of steady-state conditions and because water recovery is too low (Schrader 2005, Fuchs 2005, Judd 2003). However, when used in conjunction with the biological process, biological process converts

dissolved organic matter into suspended biomass, reducing membrane fouling and allowing recovery to be increased. On the other hand, the membrane filtration process introduced into bioreactors not only replaces the settling unit for solid–liquid separation but also forms an absolute barrier to solids and bacteria and retain them in the process tank, giving rise to several advantages (see section 5.4) over the CAS.

5.1 Brief history of the MBR technology development

The progress of membrane manufacturing technology and its applications led to the replacement of tertiary treatment steps by microfiltration or ultrafiltration. Parallel to this development, microfiltration or ultrafiltration was used for solid/liquid separation in the biological treatment process. The original process was introduced by Dorr-Olivier Inc. who combined the use of an activated sludge bioreactor with a crossflow membrane filtration loop (Smith 1969). By pumping the mixed liquor at a high pressure into the membrane unit, the permeate passes through the membrane and the concentrate is returned to the bioreactor. The idea of replacing the settling tank of the CAS process was attractive; but it was difficult to justify the use of such a process because of the high cost of membranes, low economic value of the product (tertiary effluent) and the potential rapid loss of performance due to fouling. The first generation MBRs only found applications in niche areas with special needs like isolated trailer parks or ski resorts, for example. The breakthrough for the MBR, however, came in 1989 by submerging the membranes in the reactor itself and withdrawing the treated water through membranes (Yamamoto 1989). In this development, membranes were suspended in the reactor above the air diffusers. The diffusers provided the oxygen necessary for treatment to take place and scour the surface of the membrane to remove deposited solids (Visvanathan 1997, Chiemchaisiri 1993, Kayawake 1991).

Two broad trends have emerged today, namely submerged MBRs and sidestream MBRs. Submerged technologies tend to be more cost effective for larger scale lower strength applications, and sidestream technologies are favored for smaller scale higher strength applications. The sidestream MBR envelope has been extended in recent years by the development of the air lift concept, which bridges the gap between submerged and crossflow sidestream MBR, and may have the potential to challenge submerged systems in larger scale applications (Pearce 2008). **Figure 23** presents simplified schematics of MBR formats.

Along with aerobic MBRs, anaerobic MBRs (AnMBR) were also developed. Anaerobic biological treatment systems can offer a number of advantages over their anaerobic counterparts (Berube 2006). The operational costs associated with anaerobic systems are typically lower than with aerobic systems, and anaerobic systems also generate less waste sludge. In addition, the energy associated with the biogas produced during anaerobic biological treatment can be recovered. On the other hand, it may be possible to overcome some of the treatment limitations of anaerobic systems by coupling with membrane separation. For instance, in case of low-strength wastewater treatment, the biomass growth yield and growth rate are relatively low, resulting in a low overall net biomass production. The net biomass production must exceed the net biomass loss to the effluent for a biological treatment system to function properly. However, in conventional anaerobic biological treatment systems, the net biomass loss to the effluent is governed by the relatively poor settling characteristics of the biomass. In AnMBR it is possible to maintain an adequate biomass concentration. Again, although anaerobic biological treatment systems can effectively remove the bulk of the organic contaminants present in a wastewater, they are typically not effective at removing residual levels of soluble and colloidal organic contaminants. In AnMBR residual organics can be retained in the system independently of the

hydraulic throughput, enabling these contaminants to be hydrolyzed and biodegraded (Stuckey 2003).

The first test of the concept of using membrane filtration with anaerobic treatment of wastewater appears to have been reported by Grethlein (1978). The first commercially-available AnMBR was developed by Dorr-Oliver in the early 1980s for high-strength whey processing wastewater treatment. That process, however, was not applied at full scale, possibly due to high membrane costs (Sutton 1983). The Ministry of International Trade and Industry (MITI), Japan launched a six year R&D project named “Aqua-Renaissance ‘90” in 1985 with the particular objective of developing energy-saving and smaller foot-print water treatment processes utilizing side stream anaerobic MBR to produce reusable water from industrial wastewater and sewage. However, it was difficult to significantly reduce the energy consumption by adopting the side stream operation using a big recirculation pump (Yamamoto 2009). The ADUF (anaerobic digestion ultrafiltration) process developed in South Africa in 1987 for industrial wastewater treatment (Ross 1992) is perhaps the only example of current AnMBR utilization. However, recently there has been a resurgence of interest in submerged AnMBRs (Judd 2008). This chapter will focus on aerobic MBRs. Further details on AnMBR can be derived from the comprehensive review by Liao (2006) and Berube (2006).

5.2 Market value and drivers

MBR costs have declined sharply since the early 1990's, falling typically by a factor of 10 in fifteen years. As MBR technology has become accepted, and the scale of installations has increased, there has been a steady downward trend in membrane prices, which is still continuing. Driven principally by legislation and water stress, the global MBR market is expected to display double-digit growth (Hanft 2008). Legislation is the primary driving force in Northern Europe

and parts of the United States and Canada, while in other parts of the world, notably, China, India, Australia and the Middle East, water stress is the dominant issue. Legislation has always been one of the strongest drivers for advanced water treatment solutions, such as MBR systems, in developed regions such as Europe and North America. It is now becoming an influential factor in the Indian and Chinese markets as well. Another strong driver for the expansion of the MBR market has been the increasing level of water stress, particularly in the arid regions of Australia and the Pacific Rim, the Middle East, parts of South Africa and North America and Southern Europe. Besides these two key market drivers, increased funding and incentives allied with decreasing costs and a growing confidence in the performance of the technology are contributing to the expansion of MBR market.

The global market for membrane bioreactor technology doubled over a 5-year period from 2000 to reach a market value of \$217 million in 2005, this from a value of around \$10 million in 1995 (**Figure 24**). The global market was estimated to increase from \$217 million in 2005 to \$296 million by the end of 2008 and further to \$488 million in 2013, corresponding to a compound annual growth rate (CAGR) of 10.5% (Hanft, 2008). Most MBRs use aerobic microbial processes, which are expected to be worth \$291 million in 2008 and \$483 million in 2013, a CAGR of 10.7%. Municipal and domestic wastewater treatment generated \$96.6 million in 2005. Values of \$142 million and \$249 million were projected for 2008 and 2013, respectively, with a CAGR of 11.9% in this segment. Growth rates of MBR systems are not the same for all regions and are not increasing from the same base. Common to all regions, however, is the fact that sales of the technology are growing faster than the gross domestic products of countries installing the systems and more rapidly than the industries that use them.

In Europe, the total MBR market for industrial and municipal users was estimated to have been worth €25.3 million in 1999 and €32.8 million in 2002 (Frost 2003). In 2004, the European MBR

market was valued at \$57 million (Frost 2005). Market projections for the future indicated that the 2004 figure is expected to rise annually by 6.7%, with the European MBR market more than doubling its size by 2011 (Frost 2005). Market analysis conducted by Frost (2004a) revealed that revenues in the US and Canadian membrane bioreactor (MBR) markets totalled US\$32.2 million in 2003, and are projected to reach \$89.0 million in 2010. In fact, the US and Canadian MBR market achieved a revenue totalling over \$750 million from membrane-based water purification, desalination and waste treatment in 2003, and it was projected to reach \$1.3 billion in 2010 (Frost 2004a, b, c). According to some analysts, the MBR market in the USA is growing at a significantly faster rate than other sectors of the US water industry, such that within some sub-sectors, such as the filtration market, technologies like membrane filters or ultraviolet radiation are growing at rates in excess of 15% (Maxwell 2005).

The Asia Pacific region has emerged as a strong market for MBR systems, following the established markets in North America and Europe, and could become one of the most promising and largest regional markets by 2010.

5.3 Commercially available MF/UF membranes for MBR

This section will examine the commercial MF/UF membrane systems for water treatment in general and the membranes for MBR in particular.

5.3.1 Membrane geometry used

The configurations of membranes used for MBR are based on either planar or cylindrical geometry. Principal membrane configurations currently employed in practice are:

Hollow fiber module: In HF module, either large amounts of hollow fibers make a bundle or single fibers are mounted horizontally (**Figure 25**), and the ends of the fibers are sealed in epoxy block connected with the outside of the housing. The water can flow from inside to the outside of

the membrane or from outside to the inside. These membranes can work under pressure and under vacuum.

Plate-and-frame membrane modules: Plate-and-frame membrane modules comprise of flat sheet (FS) membranes with separators and/or support membranes. The pieces of these sheets are clamped onto a plate. The water flows across the membrane and permeate gets collected through pipes emerging from the interior of the membrane module in a process that operates under vacuum.

HF and FS modules are mostly immersed directly in mixed liquor with permeate drawn through the membranes using vacuum pumps.

Tubular membranes: Typically, tubular membranes are encased in pressure vessels and mixed liquor is pumped into them. These are predominantly used for side-stream configurations.

5.3.2 Mode of operation: Inside-out vs. Outside-in flow

Inside-out flow and outside-in flow refers to the direction of feed water passing through the membrane, as well as the orientation of the feed water in relation to the membrane surface. For example, in an outside-in system, the feed water surrounds the membrane, and the filtrate is collected from inside of the hollow tube fibers (lumen). The outside-in scheme has the advantage of a larger membrane surface area, which allows for a slightly higher flow than the inside-out model while still maintaining the same flux rate and solids concentration. An inside-out system places the feed water inside the fibers, and the filtrate is collected on the outside of the membranes. The feed water enters the fibers at one end of the membrane element, and the discharge passes through the element and exits the fibers on the other side. The filtrate is collected inside the element on the outside of the fibers. The submerged hollow fiber and flat

sheet membranes follow outside-in and sidestream tubular membranes follow inside-out operation.

5.3.3 Membrane material and material properties

Membranes can be manufactured in a wide variety of materials. These materials differ in their performance characteristics including mechanical strength, fouling resistance, hydrophobicity, hydrophilicity, and chemical tolerance.

Hydrophobicity vs. Hydrophilicity

Membrane materials can be classified as either hydrophilic or hydrophobic. Hydrophilic materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophobic membrane materials have little or no tendency to adsorb water. Water tends to "bead" on hydrophobic surfaces into discrete droplets.

The hydrophilic and hydrophobic properties of a membrane material are related to the surface tension of the material. The fundamental importance of surface tension comparison is that liquids having lower surface tension values will generally spread on materials of higher surface tension values. **Figure 26** summarizes surface tension values of some polymeric membrane materials. The higher the surface tension value of the material, the more hydrophilic the material is.

The degree of hydrophilicity or hydrophobicity influences the wettability and applied pressure requirements for water flow through the membrane. Hydrophilic membranes require less operating pressure than hydrophobic membranes. Particles that foul in aqueous media tend to be hydrophobic. Hydrophobic particles tend to cluster or group together to form colloidal particles because this lowers the interfacial free energy (surface tension) due to surface area exposure. General tendency will favor particle attachment to any material less hydrophilic than water

because less exposure of hydrophobic particles can be achieved by attachment of the particles to the membrane surface. Accordingly, hydrophilic membranes tend to exhibit greater fouling resistance than hydrophobic membranes.

5.3.4 Features of commercial MBR Technologies

As stated earlier, the first generations MBRs in wastewater treatment used a sidestream format, in which feed was pumped from the bioreactor through an external membrane system. This approach was suitable for the early stage, small scale applications for difficult-to-treat feeds. An alternative format was developed in the 1990s using modules submerged in the bioreactor tank, or in an adjoining compartment. This was much more cost effective for treating larger scale flows with more easily treatable wastewater.

The submerged format is available with modules either in a flat sheet configuration or as hollow fibers or capillary membranes. Originally, the favored concept was to submerge the modules directly into the bioreactor for simplicity. However, in order to gain better control of the balance between the biological and filtration treatment capacity it is now more common to use the membrane in an external membrane tank (Brow 2007). The external arrangement allows the size and design of the membrane tank to be optimized independently, with the practical advantages for operation and maintenance. Almost all submerged MBRs are either vertically oriented PVDF HF modules of outside diameter predominantly between 2 and 2.8 mm, or FS rectangular membranes 1-1.2 m in depth with a membrane separation between 6 and 10 mm, the exceptions being:

- the Huber VRM rotating membrane module,
- the Mitsubishi Rayon horizontal *Sterapore* membrane, which is a horizontally oriented PE, and
- the Koch-Puron membrane (PES), the Polymem (PS) and the Ultraflo (PAN).

The principal differences between the most common products therefore arises from:

- the membrane and panel substrate materials, in the case of the FS submerged MBRs, and
- the use of reinforcement (for the HF modules)

The sidestream approaches are also divided into two formats—the long established traditional method of cross flow, now used only for the most difficult feeds, and the newer concept of air lift, which uses air to recirculate the feed and thereby significantly reduces energy demand. With a few exceptions, both the sidestream formats use mainly tubular membranes. **Figure 27** shows the process and membrane configurations of commercial MBR technologies.

Flat sheet systems have the advantage of relatively low manufacturing cost compared to hollow fiber systems. However, packing density tends to be significantly lower than a hollow fiber system (for example by a factor of 2.5 to 3 times). Therefore, flat sheet systems tend to have a cost advantage for small to medium scale systems, whereas hollow fiber becomes more attractive at large scale due to the footprint advantage (Pearce 2008). The comparison is made more complicated, however, since aeration costs for hollow fiber systems are often lower. This means that the most cost effective solution for total treatment costs at medium scale is closely contested, and both approaches are found across the size range due to site specific circumstances which could favor either solution. Air lift technology has a similar power cost to the submerged technology.

Figure 28 depicts the membrane system design principles followed by different membrane companies for submerged MBR.

5.4 Advantages of MBR over CAS

The combination of activated sludge with membrane separation in the MBR results in efficiencies of footprint, effluent quality and residuals production that cannot be attained when these same processes are operated in sequence. The advantages offered by the MBR process over CAS processes are widely recognized, and of these the ones most often cited are (Judd 2008):

- Production of high quality, clarified and largely disinfected permeate product in a single stage; the membrane has an effective pore size $<0.1\ \mu\text{m}$ – significantly smaller than the pathogenic bacteria and viruses in the sludge.
- Independent control of solids and hydraulic retention time (SRT and HRT, respectively). In a CAS separation of solids is achieved by sedimentation, which then relies on growth of the mixed liquor solid particles (of flocs) to a sufficient size ($>50\ \mu\text{m}$) to allow their removal by settlement. This then demands an appropriately long HRT for growth. In an MBR the particles need only be larger than the membrane pore size.
- Operation at higher mixed liquor suspended solids (MLSS) concentrations, which reduces the required reactor size and promotes the development of specific nitrifying bacteria, thereby enhancing ammonia removal.
- Reduced sludge production, which results from operation at long SRTs because the longer the solids are retained in the biotank the lower the waste solids (sludge) production.

Of these advantages, it is the intensity of the process (i.e. the smaller size of the plant compared to conventional treatment) and the superior quality of the treated product water that are generally most important in practical wastewater treatment applications. The MBR system is particularly attractive when applied in situations where long biological solids retention times are necessary

and physical retention and subsequent hydrolysis are critical to achieving biological degradation of pollutants (Chen 2003). **Figure 29** depicts the technical benefits of MBR.

5.5 Organics and nutrients removal in MBR

5.5.1 Removal of organic matter and suspended solids

Several investigations on treatment efficiencies of MBR and CAS processes operating under comparable conditions have shown significantly improved performance of an MBR in terms of COD, $\text{NH}_3\text{-N}$ and SS removals (Ng 2005, Holbrook 2005, Chiemchaisri 1993, Yamamoto 1989). There are several factors that may contribute to the lower organic carbon content of MBR effluents as compared to CAS processes. Côté (1998, 1997) attributed the improved COD removal to the avoidance of biomass washout problems commonly encountered in activated sludge process, as well as to complete particulate retention by the membrane. Since typical sludge concentrations for immersed MBRs are between 15 and 25 g L^{-1} , elimination of organic matter and turbidity is almost independent on SRT, and average removals normally achieved for COD and SS are over 90 and nearly 100%, respectively (Côté 1998). The robustness of MBR treatment regarding turbidity and organic matter removals was confirmed in several studies (Fan 1996). It is assumed that there is an upper limit for organic loading rate in an MBR under which degradation performance is independent of biomass concentration and organic loading rate (Rosenberger 2000).

MBR produces quality effluent suitable for reuse applications or as a high quality feed water source for Reverse Osmosis treatment. Indicative output quality include $\text{SS} < 1\text{mg/L}$, turbidity $< 0.2\text{ NTU}$ and up to 4 log removal of virus (depending on the membrane nominal pore size). In addition, it provides a barrier to certain chlorine resistant pathogens such as *Cryptosporidium* and *Giardia*. In comparison to the conventional activated sludge process which typically achieves 95%, COD removal can be increased to 96-99% in MBRs (Stephenson 2000).

5.5.2 Nutrient removal

The MBR process can be configured in many different ways depending on project-specific nutrient removal objectives. Anoxic zones before or after the aerobic treatment may be used for denitrification, depending on the effluent nitrate and total nitrogen requirements. Anaerobic zones may be used to achieve enhanced biological phosphorus removal in any of its possible configurations (Radjenovic 2008).

Because of the low growth rate and poor cell yield of nitrifying bacteria, nitrification is generally a rate-limiting step in biological nitrogen removal performance. The key requirement for nitrification to occur is that the net rate of accumulation of biomass (and hence the net rate of withdrawal of biomass from the system) is less than the growth rate of nitrifying bacteria (Barnes 1983). Long SRTs applied in MBR prevent nitrifying bacteria from being washed out from the bioreactor, improving the nitrification capability of the activated sludge. Moreover, nitrifiers are less endangered by faster-growing heterotrophic bacteria, which are better competitors for them ammonia nitrogen ($\text{NH}_3\text{-N}$). Many studies have proven that MBR can operate as a high-rate nitrifying technology that can be applied in the nitrification of wastewater containing a high concentration of ammonia nitrogen (Gao 2004).

On the other hand, the denitrification process requires anoxic conditions. To enhance denitrification, usually an anoxic tank is added upstream from the aerated tank. Anoxic conditions can also be introduced by operating MBR in an intermittent aeration mode, even when regarding submerged MBR, which needs permanent bubbling. In the intermittently aerated MBR, ammonium is nitrified mostly to nitrate and most phosphates are removed during the aerobic period (aeration), where the accumulated nitrate is completely denitrified during the anoxic period (non-aeration), and phosphorus (P) is taken up. The net P removal is achieved by

wasting sludge after the aerobic period when the biomass contains a high level of polyphosphates (polyP) (Chung 2006).

In WWTPs, biological P removal is accomplished by introduction of an anaerobic phase in the wastewater treatment line ahead of the aerobic phase and recycling of sludge through the anaerobic and aerobic phase (Smolders 1995). Exposing mixed liquor to an anaerobic/aerobic sequence selects phosphate accumulating microorganisms (PAOs) due to a competition between PAOs and other aerobic organisms. This competition mechanism is based on a complete anaerobic uptake of the lower fatty acids by the polyP organisms (i.e., PAOs), which assures that in the aerobic phase, no fatty acids are left. The polyP organisms use the stored internal substrate during aerobic conditions while other aerobic organisms are lacking substrate. This process is usually referred to as the enhanced biological phosphorus removal (EBPR) process. EBPR process can be established in MBR treatment unit by operating it in intermittent aeration mode. Moreover, phosphorus removal will be significantly improved in an MBR by a physical retention of PAOs, whose size is typically larger than 0.5 μm . Since an MF membrane (0.2 μm) will act as a physical barrier to retain the PAOs in the reactor, sufficient biomass is provided for the EBPR mechanism to take place (Ujang 2002, Beun 2001).

Intermittently aerated MBR can achieve nitrogen and phosphorus removal by a simultaneous nitrification and denitrification, P-uptake and P-release in the same reactor in accordance with time cycle of aeration and non-aeration. Furthermore, there is an increasing interest for the application of MBR as a technology for phosphorus recycling, since the P-content of sludge is expected to increase when prolonging SRT (Lesjean 2003).

5.6 Recalcitrant industrial wastewater treatment by MBR

High organic loadings and hardly biodegradable compounds are the major characteristics of industrial waste streams that render alternative treatment techniques such as the MBR desirable (Klinkow 1998). The efficiency in the removal of the organic load depends on the type of industrial process that has been implemented and consequently on the quantity of non-biodegradable compounds.

MBRs in recent years have been proved to be effective and economically feasible for treatment of various kinds of high strength, refractory, and/or toxic wastewaters. The mechanisms of refractory chemical oxygen demand (COD) removal, however, still remain to be well-documented. This section addresses this question by providing a brief review of the studies dealing with recalcitrant industrial wastewater treatment by MBR and offers unique insights into this matter.

5.6.1 Micropollutants

Several pharmaceuticals, ingredients of personal care products and so-called endocrine disrupting compounds (EDCs) are detected in surface waters all over the world. Most of those compounds are of anthropogenic origin and wastewater treatment plant (WWTP) effluents are important point discharges for the presence of endocrine disrupting compounds and residuals of pharmaceuticals in rivers, streams and surface waters. (Colborn 1996, Blackburn 1995, Purdom 1994).

Eight pharmaceuticals, two polycyclic musk fragrances and nine endocrine disrupting chemicals were analysed by Clara (2005) in several waste water treatment plants (WWTPs) and a pilot scale MBR. As in conventional WWTP also the removal potential of MBRs was found dependent on the SRT. Weiss (2008) found for half of the studied compounds, such as benzotriazole, 5-tolyltriazole (5-TTri), benzothiazole-2-sulfonate and 1,6-naphthalene

disulfonate (1,6-NDSA), removal by MBR was significantly better than in CAS, while no improvement was recorded for the other half (1,5-NDSA, 1,3-NDSA, 4-TTri and naphthalene-1-sulfonate). Reif (2008) reported high removal of non-sorbing but biodegradable compounds like the anti-inflammatories ibuprofen and naproxen, and moderate removal of sorbing but recalcitrant compounds; while they observed very limited removal of non-sorbing recalcitrant compounds like carbamazepine or diclofenac. Bernhard (2006) observed that non-degradable micropollutants, such as EDTA and carbamazepine were not eliminated at all during WW treatment by any technique. However, the MBR showed significant better removals compared to CAS for the investigated non-adsorbing and poorly biodegradable persistent polar pollutants (P3), such as diclofenac, mecoprop and sulfophenylcarboxylates. Schroder (2006) reported > 98 and 97.8 % removals for 4- NP and BPA, respectively in MBR and > 98 and 91.6 % removals in CAS. Mass balance proved biodegradation as the main elimination mechanism for 4-NP and BPA in both the processes.

Chen (2008) showed that MBR could remove Bisphenol-A (BPA) little more effectively than conventional activated sludge (CAS) under conditions of equal sludge loadings ranging from 0.046 to 10.2 g kg⁻¹ d⁻¹. However, MBR could bear much higher volume loadings than CAS and still achieve the same BPA removal efficiencies. The results suggested that biodegradation dominated the BPA removal process. In a study by Synder (2007) microfiltration and ultrafiltration only were found to reject very few target compounds. An MBR, on the other hand, was effective for reducing the concentration of many EDC/PPCPs, while several other compounds remained unaffected. The removal was likely related to biodegradability of the individual compound. Lyko (2005) demonstrated that the ultrafiltration membrane used in an MBR was able to partly remove the macro-molecular DOC of the wastewater, while

micropollutants tended to adsorb and associate with these removed macromolecules. In a study by Spring (2007), a pilot scale MBR was more effective at removing cholesterol, coprostanol, stigmasterol, estrogenic species (E1, EE2), and BPA to low ng/L levels than a full scale CAS plant receiving the same wastewater. In a study by Kimura (2005), compared with CAS, MBRs exhibited much better removal regarding ketoprofen and naproxen. Removal efficiencies of the PhACs were found to be dependent on their molecular structure such as number of aromatic rings or inclusion of chlorine. Urase (2005) obtained higher removal of acidic pharmaceutical substances in the case of lower pH operation because of the increased tendency of adsorption to the sludge particles. Kim (2007) found MBR system to be efficient for hormones (e.g., estriol, testosterone, androstenedione) and certain pharmaceuticals (e.g., acetaminophen, ibuprofen, and caffeine) with approximately 99% removal, but not efficient for erythromycin, TCEP, trimethoprim, naproxen, diclofenac, and carbamazepine. Radjenovic (2009) confirmed enhanced elimination of several pharmaceutical residues poorly removed by the CAS treatment (e.g., mefenamic acid, indomethacin, diclofenac, propyphenazone, pravastatin, gemfibrozil), whereas the anti-epileptic drug carbamazepine and diuretic hydrochlorothiazide by-passed both the systems. Results in a study by Gobel (2007) indicated that together with the high SRT, the low substrate loading may lead to an increased biodiversity of the active biomass in MBR, resulting in a broader range of micropollutant degradation pathways available.

In a review of the factors influencing the removal of organic micropollutants from wastewater, Cirja (2008) concluded that hydrophobic compounds are removed from the liquid phase via adsorption, and possibly through biodegradation processes when the SRT is high enough. Owing to the compactness of MBR plant and the high organic load that can be applied, this process is

promising concerning the removal of micropollutants, which are eliminated at high SRT and biomass concentration.

5.6.2 Dye wastewater

Large amounts of dyes are annually produced and applied in many different industries, including the textile, cosmetic, paper, leather, pharmaceutical and food industries (Lourenco 2001). The release of colored wastewater in the ecosystem is a remarkable source of esthetic pollution, eutrophication and perturbations in aquatic life. Virtually all the known physico-chemical and biological techniques have been explored for decolorization (Hao 2000), none has emerged as a panacea (Hai 2007).

While treating real textile dye wastewater, You (2006) observed removal efficiencies of 54, 79, 99, and 100%, for color, COD, BOD, and SS, respectively with the MBR process as compared to the corresponding values of 51, 70, 96, and 60% for a sequencing batch process. As compared to an extended aeration biological process Malpei (2003) obtained higher COD removal and colour abatement, besides much higher removal efficiency for suspended solids and microorganisms in MBR. While running a pilot MBR plant in parallel to one existing WWTP (activated sludge + clariflocculation + ozonation) for the treatment of textile wastewater, Lubello (2005) observed higher COD and SS removal, similar color removal and slightly lower surfactant removal in the MBR. Based on another study, Lubello (2007) summarized the relative advantages of the MBR system compared to the conventional WWTP as follows: lower effluent COD value; very little standard deviation of the effluent quality; no problems due to filamentous microorganisms; complete nitrification, and heterotrophic bacteria growth without the need to add nutrients due to the biomass retention in the MBR. Brik (2006) observed a distinct relationship between sludge growth and colour removal, suggesting dye removal predominantly by adsorption on sludge and

proposed post treatment by nanofiltration for water reuse. In a study by Schoeberl (2004) a combination of a membrane bioreactor and subsequent nanofiltration proved to meet all requirements for reuse.

Yun (2006) observed an opposite tendency in treatment efficiency between COD and dye as a function of DO level and suggested that an alternative operation of aerobic and anoxic phases is indispensable to efficiently biodegrade both COD and dye molecules in dye wastewater treatment with MBR. Using an adapted biomass Badani et al. (2005) obtained 97% COD and 70% color reduction in an MBR. Hai et al. (2006a, 2008b) developed a submerged membrane fungi reactor for excellent color and TOC removal.

5.6.3 Tannery wastewater

The high complexity of the tannery wastewater matrix originates from a wide range of components such as: raw materials (skins) residues, excess dosage of reagents, tanning agents, dyes and surfactants (Munz 2008). The choice of the treatment process is strictly related to the presence of significant fractions of slowly hydrolysable and inhibiting compounds requiring technologies such as MBR, which increase the sludge age and consequently the capacity to degrade substrates usually not biodegraded in conventional wastewater treatment plants.

In a study by Munz (2008), as compared to CAS, MBR showed a higher COD removal (+4%) and a more stable and complete nitrification while treating the same tannery wastewater. Artiga (2005) reported about 86% COD removal from tannery wastewater in an MBR. Chung (2004) reported 50% as the optimum ratio of the volume of anoxic denitrification tank to aerobic nitrification tank to treat tannery wastewater in MBR. It was also found that supplementation of phosphorus to maintain COD:T-P ratio of 100:1 was needed to achieve the best performance.

5.6.4 Landfill leachate

Landfill leachate can broadly be defined as the liquid produced from the decomposition of waste and infiltration of rainwater in the landfill (Keenan 1984). Improvements in landfill engineering are aimed at reducing leachate production, collection and treatment prior to discharge (Farquhar 1989). Nitrification is generally readily achievable, with >95% removal of ammonia reported through the exclusive application of biological techniques to the treatment of both young and old leachates (Ahn 1999, Welander 1998, Horan 1997). However, COD removal is considerably more challenging, with removal efficiency values from 20% to over of 90% reported according to leachate characteristics (origin and age), process type and process operational facets (Ding 2001, Timur 2000, Garcia 1996).

In view of the high strength of the landfill leachate, Visvanathan (2007) utilized an aerobic thermophilic MBR and demonstrated an average COD removal of 62–79% with gradual increase in BOD supplementation. Laitinen (2006), while treating landfill leachate by a sequencing batch reactor (SBR) and a submerged MBR reported that MBR effluent was significantly better in quality and had lower variations. Alvarez-Vazquez (2004) presented a critical assessment of data from existing plants where MBR-based treatment schemes appeared to achieve greater mean COD removal (80%) across all installations, for less biotreatable feed waters (BOD/COD = 0.03–0.16), than conventional systems which achieve COD removals of around 63% at feed water BOD/COD ratios of 0.21–0.3. Moreover, they do so at generally lower HRTs, and thus correspondingly higher loading rates ($1\text{--}3 \text{ kg CODm}^{-3} \text{ d}^{-1}$ compared with less than $0.25 \text{ kg CODm}^{-3} \text{ d}^{-1}$ for conventional treatment schemes) and so lower footprints.

5.6.5 Oil contaminated wastewater

The composition of the wastewater from petroleum refinery is a function of the processing units involved and generally contains: hydrocarbons (aliphatic or aromatic), phenolic compounds (phenol, methylphenol, dimethylphenol), sulphur, mercaptans, oil, solvents or chlorines (Eckenfelder 1992). Bienati (2008) demonstrated that MBR was able to treat industrial oil contaminated wastewater with high removal efficiency (about 98%), under short HRT (about 10 h) and high biomass concentration. The results from the study conducted by Rahman (2006) who employed a crossflow MBR showed a COD removal efficiency of more than 93% from refinery wastewater with limited influence of HRT. Trials in an MBR with a high activated sludge concentration of up to 48 g L^{-1} showed that oily wastewater also containing surfactants was biodegraded with high efficiency (Scholz 2000). Moreover, Sutton et al. (1994) designed and operated a cost-effective full-scale MBR system that can be expected to perform technically at a level equal to or better than a conventional oily wastewater treatment system.

Olive mill wastewater (OMW) is a foul smelling phenol-rich, acidic wastewater with high organic load (BOD up to 100 g L^{-1} , COD up to 200 g L^{-1}) (Saez 1992). Dhaouadia (2008) observed complete phenols removal, but moderate total COD removal from OMW in an external ceramic MBR, indicating post treatment requirements. Conversely, while treating a high phenol containing wastewater, Barrios-Martinez (2006) confirmed a phenol-free permeate along with 50 g day^{-1} phenol degradation in the MBR containing acclimatized biomass. While treating dissolved air flotation (DAF) pretreated pet food wastewater, Kurian (2005) observed the following COD and Oil & Grease removal efficiencies: thermophillic MBR (75-98%, 66-86%) and conventional MBR (94%, 98%), respectively, and high concentrations of VFA, equivalent to 50-73% of total COD, were recorded in the thermophillic MBR effluent. In an MBR with submerged multi-channel flat sheet ceramic membranes Blocher (2004), while working with

degreasing solutions from surface refining processes, achieved retention and subsequent biodegradation of hydrocarbons, while the membrane allowed relatively high permeation of the surfactants for reuse.

5.6.6 Insight into recalcitrant compound removal in MBR

Studies suggest that build up of heterotrophic bacteria having special degrading capacity (Claudia 2008, Gobel 2007, Lubello 2007) or easier acclimatization (Dhaouadia 2008, Barrios-Martinez 2006) is possible in MBR due to the complete retention of biomass by membrane and application of longer SRT. Accordingly better and/or stable removal performance may be expected in MBR.

For moderate to considerably biodegradable compounds, the volumetric biodegradation rate in MBR may improve due to high biomass concentration (Blocher 2004). However, that may not be the case for the hardly biodegradable or non-biodegradable compounds (Clara 2005). As in conventional process the removal potential in MBRs also depends on the SRT. However, MBRs achieve a high SRT within a compact reactor. Conversely, other studies have reported that MBR is neither superior for well degradable compounds that are already extensively degraded in conventional treatment nor for recalcitrant compounds that are not amenable to biodegradation (Weiss 2008, Bernard 2006). However, they agreed that for most compounds of intermediate removal in conventional treatment, the MBR is clearly superior.

The membrane filtration step provides an effluent with high quality in terms of suspended solid; hence the recalcitrant compounds adsorbed on suspended solid remains within the retentate phase where they may undergo biodegradation (Urase 2005). At times, significant retention of soluble organics on the cake-layer over the membrane and subsequent biodegradation may occur (Yun 2006, Hai 2006a).

5.7 Recent advances in membrane bioreactors design/operation

Several interesting modifications to conventional design of MBR have been proposed in the literature in order to enhance removal performance and/or mitigate membrane fouling. These include bioaugmented MBR (Qu 2009, Hai 2006a, Ghyoot 2000), settling-enhanced inclined plate MBR (Xing 2006), integrated anoxic-aerobic MBR (Chae 2006 a,b, Hai 2006b, 2008a), compact Jet-loop-type MBR (Park 2005, Yeon 2005), biofilm MBR (Hai 2008b, Ngo 2008, Leiknes 2007, Lee 2006), MBR followed by reverse osmosis (RO) or submerged nanofiltration MBR (Choi 2007, Qin 2006, Choi 2002), forward osmosis MBR (Achilli 2009, Cornelissen 2008) and membrane distillation bioreactor (Phattaranawik 2009, 2008).

5.8 Development challenges

MBR technology is facing some research and development challenges (Figure 30). Among the challenges underscored by the experts, membrane fouling is one of the most serious problems that have retarded faster commercialization of MBR technology. Two other issues closely related to membrane fouling and performance are: requirement of mechanical pretreatment and maintaining membrane integrity.

- Membrane fouling

Membrane fouling and its consequences in terms of plant maintenance and operating costs limit the widespread application of MBRs (Le-Clech 2006). Membrane fouling can be defined as the undesirable deposition and accumulation of microorganisms, colloids, solutes, and cell debris within pores or on membrane surface (Meng 2009). It results from the interaction between the membrane material and the components of the activated sludge liquor, which include biological flocs formed by a large range of living microorganisms along with soluble and colloidal compounds. Thus it is not surprising that the fouling behavior in MBRs is more complicated than that in most membrane applications. The suspended biomass has no fixed composition and varies both with feed water composition and MBR operating conditions employed.

All the parameters involved in the design and operation of MBR processes have an influence on membrane fouling (Le-Clech 2006, Meng 2009). Three main categories of factors can be identified—membrane and module characteristics, feed and biomass parameters and operating conditions.

When the operating flux is below the critical flux, particles accumulation in the region of membranes can be effectively prevented. However, due to physicochemical solute-membrane material interactions, the membrane permeability will decrease over time, even when MBRs are operated in sub-critical (below critical flux) conditions. Techniques used to remove fouling includes physical cleaning (permeate backwashing, air backwashing, relaxation, sonification etc.) and chemical cleaning. Certain other measures can be adopted to limit fouling. These include membrane modification (optimization of membrane characteristics, membrane module design etc.), optimization of operating conditions like aeration, SRT etc., and modification of

biomass characteristics (developing aerobic granular sludge, addition of adsorbent/ flux enhancers/ coagulant etc.).

- Pre-treatment requirement

Pre-treatment is one of the most critical factors for ensuring a stable and continuous MBR operation. Because of membrane sensitivity to the presence of foreign bodies, fine pre-screening of the feed (and sometimes of the mixed liquors) must occur. The type of sieve installed is very important regarding the total screening of hair and fibers. (Frechen 2006, Schier 2009). The fact that even intensive long-term pilot plant trials can fail to suggest the effective scale up design of the sieve (Melin 2006) adds to the problem.

- Maintaining membrane integrity

A major problem facing MBR systems is the loss of membrane integrity, which leads to the permeate quality deterioration and ineffective backwashing. This may be caused by faulty installation, frequent and/or extended contact between membrane and cleaning solution causing delamination of the membrane, scoring and cleaving of the membrane resulting from the presence of abrasive or sharp-edged materials in the influent, and operating stress and strain occurring in the system due to fiber movement and membrane backwashing. A better understanding of the effect of membrane material, age and fouling on membrane integrity may be gained from hollow fiber tensile test reported in the literature (Childress 2005, Pilutti 2003).

5.9 Future research

Future research in MBRs is likely to focus on reduction in energy demand through more frugal use of membrane aeration in immersed systems (Judd 2008). This will rely on a better understanding of membrane channel clogging and chemical cleaning. Lesjean (2004) opined that academic research is addressing only some of the crucial issues. For instance, while many

publications on fouling are being produced and some cost studies are conducted, no significant research efforts have addressed membrane lifespan, pretreatment and scale-up issues. Yamamoto (2009) contends that in addition to the alleviation of the technology bottlenecks, a radical shift from the conventional concept of ‘organic wastewater treatment’ to ‘water/biomass production’ is necessary. This can be materialized by developing next generation MBRs where the membrane acts as a separator of water and biomass, and biomass is utilized for energy production (**Figure 31**).

6 Conclusion

In this review membrane reactors and bio-reactor have been introduced and discussed. A Membrane Reactor (MR) is a (multi-phase) device in which reaction and separation (through a membrane) take place simultaneously. MR can be used either to increase the conversion (circumventing equilibrium limitations via Le Chatelier principle) or to increase the selectivity (through distributive feeding of a reactant through the membrane). The core of the MR is the membrane, which can be either organic and inorganic, porous or dense. In the following chapters, the preparation methods of various membranes to be used in membrane reactors will be discussed. In this review the different membrane reactors (packed bed, fluidized bed, micro, hollow fiber) have been discussed for various processes (e.g. hydrogen production, syngas production etc.).

Membrane Bioreactor (MBR) process is a hybrid system amalgamating membrane separation with biological treatment. Right from its inception, the MBR technology became a dependable option for high strength wastewater treatment. Over the past decade, submerged membrane bioreactor (MBR) processes have experienced unprecedented growth also in domestic and

municipal wastewater treatment owing to several advantages including excellent effluent quality, low sludge production, small foot print, and flexibility in future expansion. The superiority of the MBR lies in the fact that it is compatible with a variety of post treatments. This paves the way for designing effective hybrid systems having the MBR as the core, for water reuse. New studies in this field are expected to tackle the development challenges illustrated here.

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Table 1 Advantages & disadvantages of inorganic membranes with respect to the polymeric ones.

Advantages	Disadvantages
Long-term stability at high temperatures	High capital cost
Resistance to harsh environments (chemical degradation, pH, etc.)	Embrittlement phenomenon (in the case of dense Pd membranes)
Resistance to high pressure drops	Low membrane surface per module volume
Inertness to microbiological degradation	Difficulty of achieving high selectivities in large scale microporous membranes
Easy cleanability after fouling	Generally low permeability of the highly hydrogen selective (dense) membranes at medium temperatures
Easy catalytic activation	Difficult membrane-to-module sealing at high temperature

Table 2 Advantages and disadvantages of different kind of membrane housing.

FIGURE	MEMBRANE MODULE	ADVANTAGES	DISADVANTAGES
Flat Sheet/ Plate and frame	<ul style="list-style-type: none"> • Moderate membrane surface/volume ratio • Well-developed equipment • Easy membrane replacement 	<ul style="list-style-type: none"> • Susceptible to plugging at flow stagnation points • Difficult to clean • Expensive
Spiral wound	<ul style="list-style-type: none"> • Compact • Good membrane surface/volume ratio • Minimum energy consumption • Low capital/operating cost 	<ul style="list-style-type: none"> • Not suitable for very viscous fluid • Difficult to clean • Faulty membrane – change whole module
Hollow fibre	<ul style="list-style-type: none"> • Compact • Excellent membrane surface/volume ratio • Low energy consumption 	<ul style="list-style-type: none"> • Susceptible to end-face fouling • Susceptible to plugging by particulates • Single fibre damage – replace entire module
Tubular	<ul style="list-style-type: none"> • Easy to clean • Feed stream with particulate matter can be put through membrane • Good hydrodynamic control • Individual tubes can be replaced 	<ul style="list-style-type: none"> • Relative high volume required for unit membrane area • High energy consumption • Relatively expensive

Table 3 The operative conditions and the performances of MRs used to carry out the steam reforming reaction of biosources.

Bioethanol steam reforming						
Authors, reference	Membrane	Catalyst	Temperature [°C]	Pressure [bar]	Hydrogen recovery [%]	Conversion [%]
Gernot <i>et al.</i> (2006)	Composite Pd-based	BIOSTAR	600			100
Ethanol steam reforming						
Basile <i>et al.</i> (2006a, 2008b) and Gallucci <i>et al.</i> (2007b)	Dense Pd-Ag	Ru-Al ₂ O ₃	400	1.3		99
Methanol steam reforming						
Wieland <i>et al.</i> (2002)	Pd ₇₅ Ag ₂₅ Pd ₆₀ Cu ₄₀ Pd/V/Pd		300	25	96 78 -	
Basile <i>et al.</i> (2005)	Dense Pd-Ag	Cu/ZnO/Al ₂ O ₃	250	1.3		80
Basile <i>et al.</i> (2006b, 2007b)	MR1	Ru-Al ₂ O ₃	350 600	1.3		30 100
	MR2		350 550			45 65
	MR3		350 450			87 100
Basile <i>et al.</i> (2008c)	Dense Pd-Ag	CuOAl ₂ O ₃ ZnO MgO	300	1.3		100
Damle (2009)	Pd-Ag	WGS catalyst	450	5.2	15	76
			550	5.2	45	73
				7.9	50	72
				11.4	53	71
			600	11.4	60	75
Bioglycerol steam reforming						
Iulianelli <i>et al.</i> (article in press)	Dense Pd-Ag	Co/Al ₂ O ₃	400	4.0	60	94
Dimethyl ether steam reforming						
Park <i>et al.</i> (2008)	Composite membrane	Cu/Al ₂ O ₃	350 450			50 100
Acetic acid steam reforming						
Basile <i>et al.</i> (2008d)	Dense Pd-Ag (MR1)	Ni-Al ₂ O ₃	400 450	2.5	32 36	100 100
	Dense Pd-Ag (MR2)	Ni-Al ₂ O ₃ / Ru-Al ₂ O ₃	400 450		26 32	92 98
Iulianelli <i>et al.</i> (2008)	Dense Pd-Ag	Ni-Al ₂ O ₃	400	4.0	70	

Table 4 Major investigators on zeolite membrane reactors (Scopus has been used for the search)

Investigator Name	Institution	Number of papers
Yeung, K.L. (King Lun)	Hong Kong University of Science and Technology	15
Dalmon, J.A. (Jean Alain)	Institut de Recherches sur la Catalyse et l'Environnement de Lyon	10
Jansen, J.C (Jacobus C.)	Delft University of Technology	9
Coronas, J. (Joaquín)	Universidad de Zaragoza	9
Menendez, M (Miguel)	Universidad de Zaragoza	7
Santamaria, J. (Jesús)	Universidad de Zaragoza	7
Gora, L. (Leszek)	Delft University of Technology	7

Table 5 Major investigators on fluidized bed membrane reactors (Scopus has been used for the search)

Investigator Name	Institution	Number of papers
Elnashaie, S.S.E.H. (Said)	Misr University for Science and Technology, Egypt	23
Grace, J.R. (John)	The University of British Columbia, Canada	15
Kuipers, J.A.M.	University of Twente, The Netherlands	12
Abashar, M.E.E. (Mohamed)	King Saud University, Saudi Arabia	6
Rahimpour, M.R. (Mohammad)	Shiraz University, Iran	5
Yan, Y. (Yibin)	Auburn University, USA	5

Table 6 Major investigators on perovskite membrane reactors (Scopus has been used for the search)

Investigator Name	Institution	Number of papers
Yang, W. (Weishen)	Dalian Institute of Chemical Physics Chinese Academy of Sciences, China	18
Wang, H. (Hai)	Ministry of Education China, School of Chemistry and Chemical Eng., China	18
Caro, J. (Jürgen)	University of Hannover, Germany	14
Kharton, V.V. (Vladislav)	Consejo Superior de Investigaciones Científicas, Spain	12
Yaremchenko, A.A. (Aleksey)	Centre for Research in Ceramics and Composite Materials, Portugal	10
Schiestel, T (Thomas)	Fraunhofer-Institut für Grenzflächen und Bioverfahrenstechnik, Germany	9

Table 7 Major investigators on hollow fibre membrane reactors (Scopus has been used for the search)

Investigator Name	Institution	Number of papers
Fane, A.G. (Anthony)	Nanyang Technological University, Singapore	5
Tan, X. (Xiaoyao)	Shandong University of Technology, China	4
Haginaka, J. (Jun)	Mukogawa Women's University, Japan	4
Li, K. (Kang)	Imperial College London, UK	4
Caro, J. (Jürgen)	University of Hannover, Germany	4
Schiestel, T. (Thomas)	Fraunhofer-Institut für Grenzflächen und Bioverfahrenstechnik, Germany	4

Table 8 Major investigators on photocatalytic membrane reactors (Scopus has been used for the search)

Investigator Name	Institution	Number of papers
Morawski, A.W. (Antoni)	Polish Academy of Sciences, Poland	11
Palmisano, L. (Leonardo)	University of Palermo, Italy	8
Molinari, R. (Raffaele)	University of Calabria, Italy	8
Tomaszewska, M. (Maria)	Polytechnic University Szczecin, Poland	5
Toyoda, M. (Masahiro)	Kyoto University, Japan	5
Thiruvengkatachari, R.	University of Technology Sydney, Australia	4

Figure 1 Poiseuille mechanism

Figure 2 Knudsen mechanism

Figure 3 Surface diffusion

Figure 4 Capillary condensation

Figure 5 Multi-layer diffusion

Figure 6 Molecular sieving

Figure 7 Hydrogen flux through palladium alloy membranes against metal content (Shu 1991).

Figure 8 Number of publications vs time.

Figure 9 Flat membrane reactor :

- i) removal of product for a limited reaction thermodynamically;
- ii) removal of favourite product;
- iii) controlled addition of reactants.

Figure 10 Classification of MRs based on the function and position of membrane (McLeary 2006).

Figure 11 Two approaches in membrane reactors (Zaman 1994).

Figure 12 Conversion of cyclohexane vs H (Keizer 1994).

Figure 13 Energy sources used in the world provided by International Energy Agency

(<http://www.eia.doe.gov/pub/international/iealf/tablee1p.xls>).

Figure 14 Conceptual scheme of a dense Pd-Ag MR.

Figure 15 Selected hydrogen production technologies from various biomass (Xuan 2009).

Figure 17 Experimental setup for partial oxidation of methanol to formaldehyde in a fluidized bed membrane reactor. Reprinted from [Deshmukh 2005b](#) with permission of ACS

Figure 18 Schematic diagram of a fluidized bed membrane dual-type Fischer–Tropsch reactor. Reprinted from Rahimpour (2009b) with permission of Elsevier.

Figure 19 Scheme of the perovskite membrane reactor for ammonia oxidation. (after Sun *et al.* (2009))

Figure 20 Schematic diagram of a tube in tube hollow fiber membrane reactor for laboratory tests.

Figure 21 Typical integrated photocatalytic membrane reactor.

Figure 22 Typical photocatalytic reactor coupled with membrane separation system.

Figure 23: Simplified representation of MBR formats
 (a) Submerged MBR, (b) Sidestream MBR, (c) Airlift MBR

Gallucci, F., Basile, A. and Hai, F. I. "Introduction—A review of Membrane reactors" in *Membranes for membrane reactors: Preparation, Optimization and Selection* (eds. Basile, A., Gallucci, F.), page 1-62, Wiley InterScience, USA, 2011.

Figure 24: Estimated MBR market value (Dotted lines indicate projected values)

Data source: Frost and Sullivan (2003, 2004, 2005); Hanft (2008)

Figure 25: Submerged membrane modules
 (a) Horizontally mounted single hollow fibers, (b) Hollow fiber bundles, (c) Flat sheet membrane module

Figure 26: Surface tension of common polymers for membrane

Note: Polymer (1. Polytetrafluoroethylene, 2. Polyvinylidene Fluoride, 3. Polypropylene, 4. Poly Vinyl Chloride, 5. Polysulfone, 6. Polycarbonate, 7. Polyacrylonitrile, 8. Cellulose)

Figure 27: Features of commercial MBR technologies

(a) Horizontally mounted single hollow-fibers (Mitsubishi Rayon)

(b) Vertically mounted reinforced hollow-fibers (Zenon)

Legend: (1) sealed ends, (2) one end freely movable membrane filters, (3) central aeration, (4) filtrate removal, (5) backwashing

Legend: (1) fiber support, (2) module element, (3) air supply, (4) module row, (5) filtrate

(c) One end free vertically mounted braid-supported hollow-fibers (Puron)

(d) Densely packed hollow-fiber bundles with unique aeration arrangement (Asahi kasei)

(e) Vertically mounted hollow-fiber bundles with unique two-phase jet cleaning arrangement (Memcor)

Figure 29: Comparative technical benefits of MBR over CAS

Figure 30: Technology bottlenecks

Figure 31: Next generation MBR system: anaerobic combination for on-site small scale advanced treatment (proposed by Yamamoto, 2009)