

Membrane assisted fluidized bed reactors: Potentials and hurdles

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Abstract

Recent advances in the development of more stable membranes with increased permeance have significantly enhanced the possibilities for integrating membranes into catalytic reactors in order to achieve a major increase in reactor performance by process integration and process intensification. Several reviews and even special issues of catalysis related journals illustrate the significant progress in the field of inorganic membrane reactors within the last two decades. Chemical engineers and material scientists have joined forces and addressed this topic from various view-points. In spite of their considerable efforts in these directions, the application of the membrane reactors, especially packed bed membrane reactors, in commercial processes has been very limited because of technical as well as economical drawbacks. The most recent trend in membrane reactor technology has been in the direction of incorporating inorganic membranes into fluidized beds to combine the perm-selective and controlled dosing capabilities of membranes with excellent gas–solid contact and heat transfer capabilities of fluidized beds, thereby overcoming the limitations often prevailing in packed bed membrane reactors.

The opportunities for this novel fluidized bed membrane reactor compared to conventional reactors and packed bed membrane reactors have never been systematically reviewed before. This paper seeks to review literature and new developments in the area of membrane assisted fluidized bed reactors, with special emphasis on possible applications, integration of different membranes in the fluidized beds, reactor modelling studies, experimental demonstration of various reactor concepts and future prospects and hurdles for commercialization. Finally, an assessment of the state of the art has been given and directions for future research are indicated.

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1. Introduction

The integration of membranes in a catalytic reactor allows to either dose one of the reactants in a controlled manner in order to achieve optimal axial concentration profiles with corresponding higher product yields (higher product selectivity at higher conversion) and simultaneously achieve improved temperature control and safety or alternatively to selectively remove one of the products, typically used to circumvent thermodynamic equilibrium.

For partial oxidation reactions a membrane reactor especially offers improved reactor safety and controllability, reduced separation costs in case of oxygen perm-selective

membranes and a wider operating range resulting in higher productivity. In the context of selectivity enhancement, additional potential benefits could arise because of the following reasons:

- A membrane can keep the bulk of two reactants separated, avoiding their premixing and consequently preventing side reactions (Veldsink et al., 1992).
- Dense membranes (e.g. Pd alloys or solid electrolyte) can supply one of the reactants in a monatomic form, particularly active towards, for instance, partial oxidations (Anshits et al., 1989), or partial hydrogenations (Gryaznov and Slin'ko, 1982; Nagamoto and Inoue, 1986).
- Porous membranes such as γ -alumina, modifies in an advantageous way the residence time and the concentration profile of the reactants in the catalytically active zone (Zaspalis, 1990; Slood, 1991; Slood et al., 1990, 1992).

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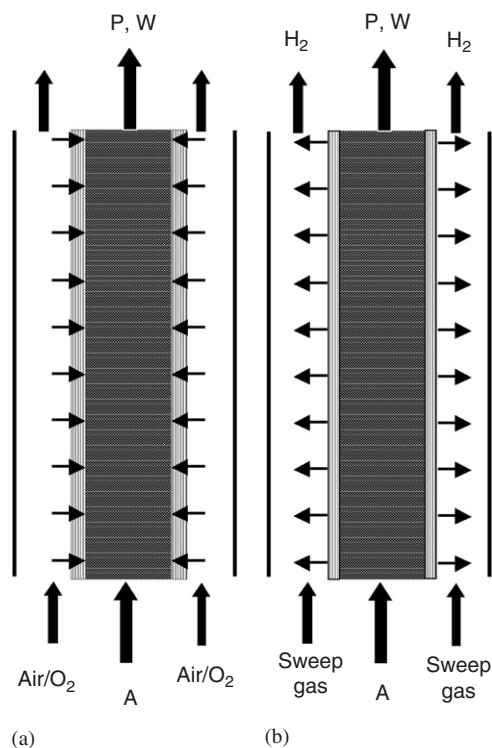


Fig. 1. Schematic of packed bed membrane reactor for: (a) controlled dosing of one of the reactants, e.g. partial oxidation or (b) removal of one of the products, e.g. dehydrogenation; A = reactant, P = product and W = waste.

The integration of membranes inside a reactor using either catalytically active membranes or membranes enclosing a conventional fixed bed of catalyst pellets (see Fig. 1), has been studied and tested experimentally for a number of different reactions and there has been a vast reviewing activity in the field of inorganic membrane reactors in the last decade, especially for packed bed membrane reactors (e.g. Tsotsis et al., 1993; Saracco and Specchia, 1994, 1998; Saracco et al., 1994; Armor, 1995; Dalmon, 1997; Saracco et al., 1999; Dixon 1999, 2003). Most of these studies were focussed on heterogeneously catalyzed gas–solid reactions, aiming either at increasing the conversion of equilibrium limited reactions, or at enhancing the product selectivity towards desired intermediate products. However, packed bed membrane reactors also possess some disadvantages:

- Relatively high pressure drop and possible mass transfer limitations because of the relatively large particle size used.
- Radial temperature and concentration gradients.
- Difficulties in reaction heat removal.
- Low specific membrane surface area.
- Inflexibility with respect to membrane and cooling tube arrangement.

These disadvantages can be largely overcome by integrating the membranes inside a fluidized bed, referred to as the membrane assisted fluidized bed reactor (MAFBR). An MAFBR is a special type of reactor that combines the advantages of a flu-

idized bed and a membrane reactor. One of the main advantages of the fluidized bed reactor is the excellent tube-to-bed heat transfer, which allows a safe and efficient reactor operation even for highly exothermic reactions. Also for highly endothermic reactions, where the hot catalyst is circulated between the reactor and the regenerator, the excellent gas–solid heat transfer characteristics of the fluidized beds can be effectively exploited. The intense macro-scale solids mixing induced by the rising bubbles results in a remarkable temperature uniformity, which exists in both the radial and the axial directions, even in beds as large as 10 m (Miracca and Capone, 2001).

By insertion of membranes in a fluidized bed a synergistic effect can be accomplished. Firstly, optimal concentration profiles can be created via controlled dosing or withdrawal and secondly, the fluidization behaviour can be improved via the presence of the inserts and permeation of the gas through the membranes, so that large improvements in conversion and selectivity might be achieved. The main advantages of the MAFBR 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 behaviour 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 of the possible disadvantages of an MAFBR are:

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

This review presents a description and evaluation of the current state of MAFBR. Despite the advances in the recent years, many challenges and difficulties still face catalytic membrane reactors. Some are technical: in particular, better materials need to be developed to address problems of membrane stability, and to reach the ultimate goal of high permeation rate combined with high perm-selectivity. Some recent work addresses commercial or economic evaluation. Three major areas of applications will be addressed, namely:

- (1) yield-enhancement of equilibrium-limited reactions: a reaction product is selectively permeating through the membrane, thereby enhancing the per-pass conversion compared to conventional reactors (see Table 1);
- (2) selectivity enhancement: accomplished by controlled addition of a reactant through the membrane (see Table 1);
- (3) miscellaneous application opportunities: a number of potential applications were recently investigated, which do not require membrane perm-selectivity to gases and therefore appear to be closer to industrial success.

Table 1
Reactions of potential interest for membrane assisted fluidized bed reactor

Reaction type	Reference
<i>Conversion enhancement</i>	
Ethane dehydrogenation	–
Propane dehydrogenation	–
Cyclohexane dehydrogenation	–
Ethylbenzene dehydrogenation	Abdalla and Elnashaie, 1995
Water-gas shift reaction	–
Methane steam reforming	Abba et al., 2003; Adris et al., 1991, 1994a,b,c; Adris and Grace, 1997; Chen et al., 2003a,b,c; Chen and Elnashaie, 2004a,b, 2005a,b,c; Gobina, 2000; Grace et al., 2001; Patil et al., 2005; Prasad and Elnashaie, 2002; Rakib and Alhumaizi, 2005
Methane partial oxidation to synthesis gas	Mleczo et al., 1996; Ostrowski et al., 1998a,b, 1999
<i>Selectivity enhancement</i>	
Oxidative coupling of methane	–
Partial oxidation of ethane to ethene	Ahchieva et al., 2005
Ethylene epoxidation	–
Partial oxidation of propane to propene	Alonso et al., 2005
Partial oxidation of propane to acrolein	–
Partial oxidation of butane to maleic anhydride	Alonso et al., 2001
Partial oxidation of butene to methacrolene	–
Partial oxidation of methanol to formaldehyde	Deshmukh et al., 2005a,b,c
CO hydrogenation to hydrocarbons	–
Oxidative dehydrogenation of ethylbenzene	–

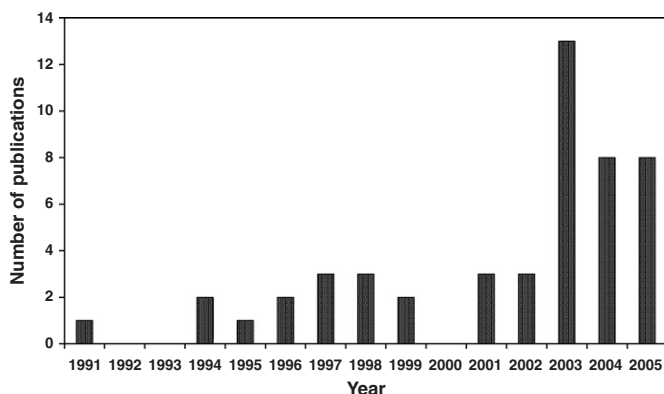


Fig. 2. The number of publications per year on membrane assisted fluidized bed reactors since 1965 included in the SciFinder Scholar database.

Our paper is based on a database search for the years 1965–2005 with the software SciFinder Scholar (2004) and with keywords “Fluidized beds and membranes”. The obtained number of publications per year is plotted for the past 15 years in Fig. 2. The results show a remarkable increase in the number of publications in the last couple of years for the fluidized bed membrane reactors. It is clear that the fluidized bed membrane reactor community is not only growing in numbers, but also widening in territorial borders. The mentioned literature will be discussed from an application point of view instead of a material point of view. The purpose of this review is to provide an interpretative review of these and other recent advances and to identify trends for the future of the MAFBR. Several trends in recent research are examined, including the application of

hydrogen perm-selective membranes in methane utilization and the use of distributed feeding to control the temperature in partial oxidations. Moreover, the research on the extent of axial gas back-mixing and temperature uniformity is reviewed. Furthermore, the modelling of fluidized bed membrane reactors is addressed. The review concludes with an example of a successful near commercialization of an MAFBR.

2. Reactor configurations

In principle, membrane assisted fluidized bed systems can be designed to operate in any of the hydrodynamic regimes of fluidization (Bi and Grace, 1995; Bi et al., 1995). However, heat-transfer and temperature uniformity considerations appear to preclude operation in the low-velocity bubble-free regime, while the need for large-scale operation and relatively small catalyst particles makes operation in the slug flow regime unlikely. Hence, the regimes to be considered are the bubbling regime, turbulent regime, and fast fluidization. The choice is likely to be dictated by competing factors such as compactness, temperature uniformity, bed-to-surface heat transfer, influence of the bed hydrodynamics on catalytic properties such as coking and limitation imposed by the erosion of the membrane surfaces and catalyst attrition especially in the turbulent or fast fluidization regime. However, so far most of the experience in membrane assisted fluidized bed has been in the bubbling bed regime (Grace and co-workers, Mleczo and co-workers, Mörl and co-workers and Kuipers and co-workers). In this paper we will focus on the MAFBR in the bubbling-bed regime. Nevertheless, it should also be noted that the turbulent and fast fluidization regimes in particular may also prove to be advantageous in certain cases and considerable research is being

undertaken by the group of Elnashaie and co-workers to develop a circulating fluidized bed membrane reactor for the steam reforming of methane and higher hydrocarbons such as heptane. More recently, Grace et al. (2005) have patented a novel internally circulating fluidized bed reformer for the autothermal production of ultra clean hydrogen. The catalyst is placed inside the reactor in two reaction zones, an endothermic dehydrogenation reaction zone and an exothermic oxidation or partial oxidation reaction zone. A mixture of steam and hydrocarbon gas is fed into the bottom of the fluidized bed to fluidize the particulate catalyst, where hydrogen is also produced, and separated through perm-selective membranes. An oxidant is introduced into the 2nd exothermic oxidation or partial oxidation reaction zone and mixed with the other gases in this zone and are directed to the endothermic dehydrogenation reaction zone.

In the MAFBR different arrangements of the membrane and heat transfer tubes in the bed have been proposed. A vertical configuration of palladium membranes for hydrogen separation has been employed by most of the researchers active in this field because of ease of construction. However, it must be noted that a horizontal arrangement of the membranes for selective removal of the product might be more effective in certain cases because it gives an extra degree of freedom to add fresh sweep gas along the axis of the reactor, by which higher hydrogen concentration gradients across the membrane tube can be accomplished. Alternatively, a multi staged fluidized bed configuration with fresh sweep gas in each stage could also be employed with a vertical membrane configuration. Analogously, horizontal tube configuration might be best suited for partial oxidation reactions, where the oxygen concentration profile can be optimized by variation of axial flow of oxygen via the membranes. Nevertheless, in most researches a vertical tube bundle arrangement was selected.

3. Applications of MAFBR

3.1. Equilibrium limited reactions (conversion enhancement)

The most extensive research on application of membrane reactors has been focussed on its applicability to overcome the thermodynamic equilibrium by selective removal of one of the products and to achieve conversions beyond the equilibrium. Fig. 3 shows a typical representation of a fluidized bed membrane reactor for selective removal of hydrogen patented by Adris et al. (1994a,b,c).

Especially for dehydrogenation reactions, the applications of perm-selective membranes show significant benefits. Since most of the dehydrogenation reactions are endothermic equilibrium reactions, high temperatures are typically required to achieve a high equilibrium conversion. However, at higher temperatures the product selectivity might decrease due to undesired side reactions or catalyst deactivation might occur due to the formation of carbonaceous deposits. By using membrane reactors, higher conversions can be obtained at low temperatures, thereby suppressing side reactions as well as coking of the catalyst.

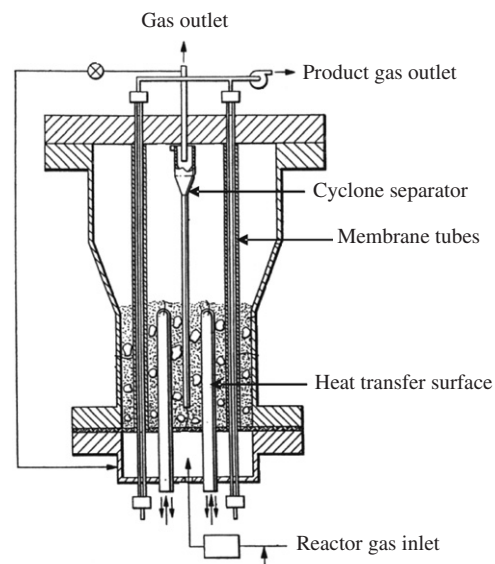


Fig. 3. Schematic representation of the fluidized bed membrane reactor for selective removal of one of the products; see the patent of Adris et al. 1994a,b,c.

The application of fluidized bed membrane reactors for different reactions of industrial importance has been investigated in the recent past. An area of much current interest is the production of hydrogen via methane steam reforming or autothermal reforming and fluidized beds are being used to solve the problems of thermal control encountered in fixed bed reactors (Adris et al., 1991, 1994a,b,c; Jarosch and de Lasa, 1999; Grace et al., 2001; Prasad and Elnashaie, 2002; Chen et al., 2003a,b,c; Patil et al., 2005). Adris et al. (1991, 1994a,b,c) demonstrated that for steam reforming of natural gas the thermodynamic equilibrium restrictions can be overcome by in situ separation and removal of hydrogen via perm-selective thin-walled palladium-based membranes leading to increased synthesis gas yields in comparison to the industrial fixed bed steam reformer. Subsequently, Grace and co-workers (Roy et al., 1999; Grace et al., 2001; Abba et al., 2003) and Elnashaie and co-workers (Chen et al., 2003a,b,c; Prasad and Elnashaie, 2002) added oxygen into these steam reforming reactors for in situ generation of heat by partial oxidation of methane to supply the energy for the endothermic reforming reaction. Prasad and Elnashaie (2002) used CO₂ sequestration using CO₂–lime reaction to assist/replace the hydrogen perm-selective membranes. The use of hydrogen separation membranes along with lime resulted in the complete conversion of methane with a high yield of hydrogen. Recently, Rakib and Alhumaizi (2005) discussed the advantages of oxygen addition for hydrogen production via the steam reforming of methane. Abashar (2004) used modelling tools to simulate the coupling of steam and dry (CO₂) reforming of methane in a catalytic fluidized bed membrane reactor. It was shown that the combined effect of the membrane and reaction coupling provides exciting opportunities to overcome the equilibrium and achieve complete conversion of methane even at low temperatures.

Elnashaie and co-workers (Chen et al., 2003a,b,c, 2004; Chen and Elnashaie, 2004a,b, 2005a,b,c) have been engaged in the

development of a steam reformer of higher hydrocarbons, using heptane as a model component, in a novel circulating dual membrane fluidized bed reformer. Palladium membranes were used to remove hydrogen and perovskite membranes were used to supply oxygen along the length of the reformer for oxidative reforming of the hydrocarbons, providing the necessary heat for the highly endothermic steam reforming reaction. The combination of these two membranes along with the characteristics of fast fluidization (negligible carbon deposition on the catalyst) made this process not only an efficient hydrogen producer, but also an energy efficient process.

Using simulations Abdalla and Elnashaie (1995) showed for the catalytic dehydrogenation of ethyl benzene to styrene that with a fluidized bed membrane reactor a higher product selectivity could be realized compared to a fixed bed reactor. With a suitable membrane tube arrangement smaller bubbles could be created, decreasing reactant bypass and with a number of fluidized beds in series the back mixing could be decreased so that the ethyl benzene conversion (max. 96.5%) and styrene yield (max 92.4%) could be even further increased. Subsequently, Elnashaie et al. (2001) developed a procedure linking kinetic modelling of catalytic reactions to reactor modelling for different reactor configurations. They used this procedure to systematically compare the performance of fixed and fluidized bed reactors with and without membranes.

Methane partial oxidation was extensively studied by the group of Mleczko and co workers and compared with packed bed reactors (Mleczko et al., 1996; Ostrowski et al., 1998a,b; Ostrowski and Mleczko, 1999). A higher selectivity of separation was found for the fluidized bed membrane reactors compared to a fixed bed membrane reactor. This was also attributed to the mass-transfer limitations between the bubble and emulsion phases that acted as a pre-filtering membrane. However, the improvement of the selectivity of separation due to the inter-phase gas exchange decreased with increasing pressure (Ostrowski et al., 1998a,b). Moreover, gas withdrawal through the membranes decreased the superficial gas velocities in the top section of the bed, resulting in smaller gas bubbles, which increased the inter-phase gas exchange favouring high conversions (Mleczko et al., 1996). Furthermore, Gobina (2000) studied the production of oxo-alcohol synthesis gas by partial oxidation of methane in a fluidized bed membrane reactor. The achieved methane conversion was significantly higher (about 6.5%) when a membrane was used. Different membranes with different membrane thickness and perm-selectivity were investigated and were found to greatly influence the syngas composition. However, the H_2/CO ratio could be adjusted close to 1 using membranes, which is more suitable for oxo-alcohol synthesis and for the production of dimethyl-ethyl-ether.

3.1.1. Coking and regeneration

Pd alloy membranes are also extremely sensitive to poisoning. CO , H_2S , SO_2 and several other compounds dramatically affect their permeability, catalytic activity and stability. A critical stage governing both permeation and reaction process is hydrogen chemisorption. According to Al-Shammary et al. (1991), this chemisorption takes place at certain active points

on the membrane surface. These points are especially prone to contamination, since the relative activation energy of the rest of the surface is considerably higher. Because of this, minute quantities of impurities can drastically modify the above properties. This hampers the application of such membranes to the treatment of several gaseous streams in the petrochemical industry, in which either gas-borne reactive species (i.e., sulphur, arsenic, chlorine, mercury, zinc, etc.) or unsaturated hydrocarbons (i.e., acetylene, ethylene, propylene and butylene) may act as contaminating agents.

Both metal and porous ceramic membranes can be frequently affected by coke deposition when dehydrogenations of hydrocarbons are carried out. Coke formation is generally favoured at high temperatures as a consequence of a number of endothermic side reactions. Sometimes the acidic nature of some of the membrane constituents (e.g., $\gamma-Al_2O_3$) catalyses these reactions. Hydrogen depletion in the reaction zone, due to the permeation of this gas through the membrane, could enhance coke formation during dehydrogenation reactions. In particular, during propane dehydrogenation runs, Van Sint Annaland (2001) observed a very pronounced effect of the hydrogen concentration on coking rates.

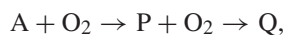
The possibilities to limit coking in the fluidized bed membrane reactor are:

- (1) Dosing of an additional component to the reactant mixture to remove the deposited carbonaceous material, e.g. oxygen addition in case of methane steam reforming or the dehydrogenation of ethane, propane and butane.
- (2) Continuous regeneration of the catalyst, such as in the circulating fluidized bed reactors. Elnashaie and co-workers have extensively studied this novel circulating fluidized bed membrane reactor. Chen et al. (2004) studied the catalyst deactivation and the influence of the steam to carbon ratio on the reformer performance for this novel reactor for steam reforming of higher hydrocarbons using mathematical models.
- (3) Preparing a new class of catalysts less sensitive towards coking. Use of oxygen or steam has been frequently proposed to reduce coking. However, oxygen may directly react with the compounds to be dehydrogenated, thus promoting the formation of new, undesired chemical species. Steam has demonstrated to reduce the membrane lifetime. Therefore, to limit coke formation, catalysts need to be developed that are intrinsically less prone to coking. For example, Matsuda et al. (1993) noticed for the isobutane dehydrogenation in a Pd membrane reactor enclosing a fixed bed of $Pt-Al_2O_3$ catalyst pellets, that the addition of tin to the catalyst could almost suppress coke formation, despite a slight decrease in catalytic activity.

3.2. Consecutive reactions (selectivity improvement)

The idea of a distributed or controlled addition of a reactant is applied to systems with consecutive reactions, where the intermediate product is of primary interest. A typical example

is the partial oxidation of hydrocarbons. The general reactions have the form:



where P is the desired product, Q is the undesired side-product and A and oxygen are the reactants. If the kinetics are interpreted in terms of a power-law form, and the oxygen is distributively fed, then selectivity towards P will increase if the reaction order in oxygen of the desired reaction is lower than the reaction order in oxygen of the undesired reaction as shown below:

$$R_A \propto C_{O_2}^n \quad \text{and} \quad R_P \propto C_{O_2}^m \quad \text{where } m > n.$$

The distributor mode is usually well adapted to limit consecutive and parallel deep oxidation reactions for the partial oxidation, oxidative dehydrogenation of hydrocarbons and the oxidative coupling of methane. For these reactions, the local oxygen concentration at the catalytic site greatly influences both the hydrocarbon conversion and product selectivity. Indeed strong oxidizing conditions promote the total combustion which is usually responsible for hot spots in packed bed reactors. Using membrane supported concepts, oxygen can be dosed in a controlled manner, so that the hydrocarbon–oxygen ratio is tuned along the catalyst bed. Provided that the kinetics of the oxidation reactions are known, an optimal oxygen partial pressure profile can be controlled along the reactor. In addition, the oxygen–hydrocarbon feed separation helps to overcome flammability and explosion limits. The O_2 perm-selectivity of the membrane is also an important economic factor because air can be used instead of pure O_2 . The extremely high perm-selectivity of dense ionic conducting ceramics, coupled with their ability to generate highly reactive/selective oxygen species, explains their impressive development for these applications over the last 15 years. However, due to the very poor conductivity/permeability of dense membranes below 800°C , further improvements are still needed for applications in the range $400\text{--}700^\circ\text{C}$ (see Julbe et al., 2005 and references therein). For reactions in this temperature range, typically non-permselective porous membranes have been used (Deshmukh et al., 2005a,b,c; Ahchieva et al., 2005). Fig. 4 shows a typical representation of a fluidized bed membrane reactor for distributive addition of oxygen via microporous hollow fibre ceramic membranes (Deshmukh et al., 2005a,b,c).

Only a limited number of applications of the MAFBR for distributive feeding of one of the reactants have been investigated and most of these applications involve the controlled dosing of air via porous membranes. Alonso et al. (2001, 2005) studied the butane partial oxidation in an externally fluidized bed membrane reactor (see Figs. 5 and 6). This novel reactor concept combined the advantages of fixed bed and fluid bed reactors. The vanadium phosphorous oxide catalyst was loaded inside a porous membrane tube into which the hydrocarbon was fed. An oxygen rich gas fluidized a powder on the shell side. Oxygen crossed the membrane wall and reacted with the butane inside the membrane tube. Butane partial oxidation to maleic anhydride was adopted as a model reaction and the

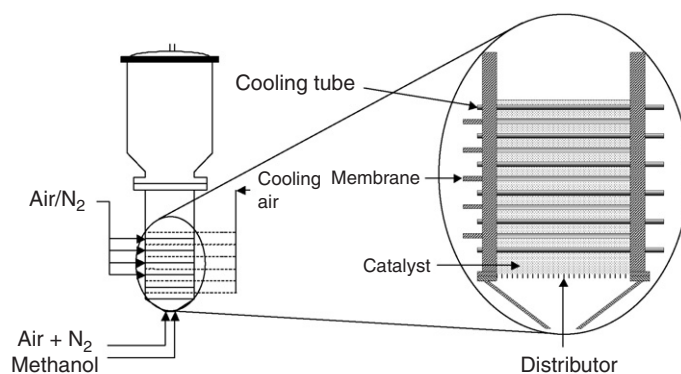


Fig. 4. Schematic representation of MAFBR for partial oxidation of methanol. Reprinted from Ind. & Eng. Chem. Res., 44 (16), Deshmukh et al., 5955–5965, Copyright (2005), with permission from American Chemical Society.

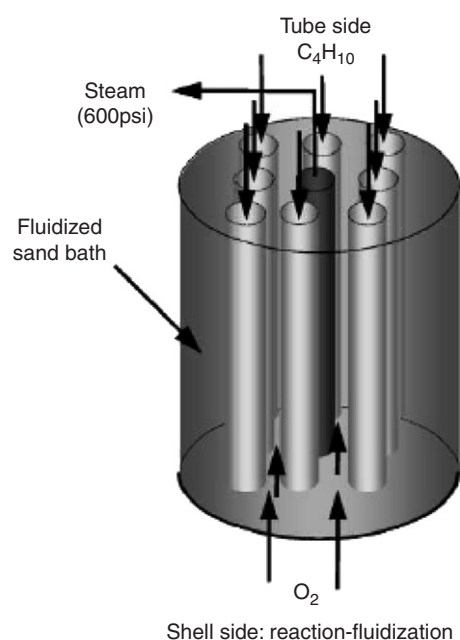


Fig. 5. Schematic diagram for an externally fluidized bed membrane reactor (EFBMR). Reprinted from Catalysis Today, Vol. 67, Alonso et al., 151–157, Copyright (2001), with permission from Elsevier.

kinetic parameters were derived based on a full scale commercial pilot plant. A detailed reaction engineering model of the EFBMR showed that hot spots were minimized and the reactor was inherently safer because the flammability potential was lower. Maleic anhydride yields were potentially 50% higher in an EFBMR compared to a conventional fixed bed reactor and the reactant concentration operating range was much wider. Ramos et al., 2001 proposed a similar concept for the partial oxidation of propane to propene. Air fluidized the shell side where catalyst filled membrane tubes and cooling coils were immersed. Oxygen transport through the membrane wall was controlled by the pressure drop. Model simulations, based on the kinetics of the oxidative dehydrogenation of propane to propene showed an improved performance compared to conventional fixed bed technology. The controlled oxygen addition along the axis improved the propene selec-

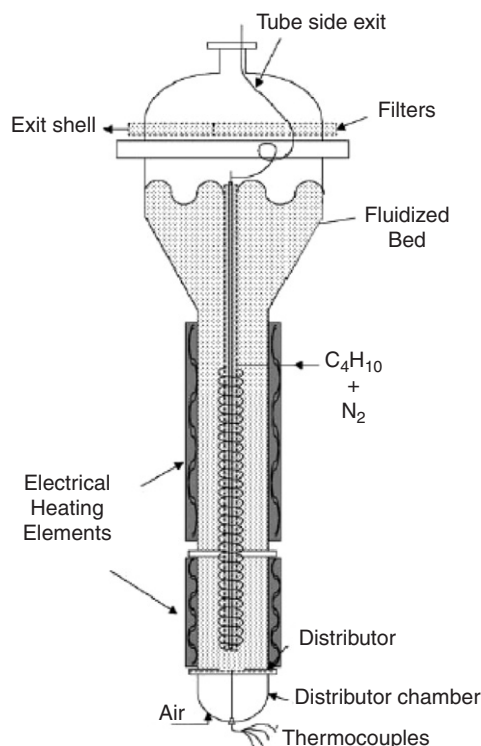


Fig. 6. Design of membrane reactor by Alonso et al. 2005. Reprinted from *Catalysis Today*, Vol. 104, Alonso et al., 177–184, Copyright (2005), with permission from Elsevier.

tivity and broadened the operating range with respect to the hydrocarbon and oxygen feed rates.

Recently, Deshmukh et al. (2005a,b,c) constructed a small laboratory-scale MAFBR for the partial oxidation of methanol to formaldehyde (see Fig. 4). Methanol conversion and product selectivities were measured at various overall fluidization velocities, reactor temperatures, methanol and oxygen overall feed concentrations, ratios of gas fed via horizontally positioned ceramic hollow fibre membranes relative to gas fed via the bottom distributor, and aspect ratios of the fluidized bed. High methanol conversions and high selectivities to formaldehyde were achieved with safe reactor operation (isothermal reactor conditions) at very high methanol inlet concentrations, much higher than that currently employed in industrial processes. It was experimentally demonstrated that with distributive feeding of oxygen in an MAFBR the overall formaldehyde yield and throughput could be increased without a pronounced and undesirable conversion of formaldehyde to carbon monoxide. Furthermore, a one-dimensional two-phase phenomenological reactor model has been developed with which the experimentally observed conversion and selectivity as a function of the operating conditions could be well described. More recently, Ahchieva et al. (2005) studied the performance of a pilot plant scale fluidized bed membrane reactor (FLMBR) for the oxidative dehydrogenation of ethane in comparison to a fluidized bed reactor, packed bed reactor and packed bed membrane reactor. Porous sintered metal tubes were vertically placed inside the fluidized bed for oxygen distribution. For identical overall feed

rates, the distributed oxygen feeding in the FLMBR improved the selectivity to ethylene significantly. The beneficial effect of oxidant dosing via the membranes was most pronounced at high temperatures and long contact times. Under moderate oxygen concentrations FLMBR outperformed the PBMR. All of the aforementioned membranes applied in the fluidized bed were porous membranes used for the controlled dosing of oxygen. However, Kuipers and co-workers (Zhang et al., 2005a,b) and Elnashaie and co-workers (Chen et al., 2003a,b,c, 2004a,b, and 2005a,b,c) have also applied dense oxygen membranes for the partial oxidation of methane and autothermal reforming of methane.

3.2.1. Safety aspects

Highly exothermic heterogeneously catalyzed gas phase partial oxidation reactions are an industrially important class of chemical transformations and require carefully designed reactors because of the large amount of reaction heat liberated and the high selectivity requirement for the intermediate product of interest. Therefore new reactor concepts like membrane reactors have been developed which offer improved reactor safety and higher product throughput via the concept of multifunctionality. However, packed bed membrane reactors (PBMRs) possess certain disadvantages. Kuerten et al. (2004) have carried out a detailed modelling study for oxygen addition in packed bed membrane reactors for partial oxidation systems and its effect on the product selectivity. They concluded that the investigation of mass transfer effects in PBMRs is very important, since due to mass transfer limitations a large part of the catalyst in a PBMR might not be used efficiently. The reduced effectiveness of the catalyst packing influences the distribution of the activity over the length of the packed bed, and thus the distribution of the released reaction heat which might ultimately affect the product selectivity and even reactor safety.

These disadvantages can be largely overcome by integrating the membranes inside a fluidized bed, with which an inherently safe and isothermal reactor operation can be achieved, especially for highly exothermic oxidation reactions, where the explosion region of the reactants or products imposes restrictions on the feed concentration of the reactants. Reactor operation can be rendered inherently safe via the distributive addition of oxygen, enabling local oxygen concentrations in the fluidized bed below the minimum oxygen concentration limit [MOC] and achieving operation outside the flammability limits of the hydrocarbons, while achieving high conversion of the hydrocarbon. It must be understood that MOC stands for the concentration of oxygen in the oxygen–hydrocarbon mixture below which no explosion can take place, regardless of the concentration of the hydrocarbons.

No specific and separate studies have been carried out to directly quantify the aforementioned advantages with respect to the safety aspects of fluidized bed membrane reactors as was done by Coronas et al. (1995) and Al-Sherehy et al. (1998) for packed bed membrane reactors. However, Deshmukh et al. (2005a,b,c) clearly demonstrated for the methanol partial

oxidation to formaldehyde that operation at methanol inlet concentrations of 20% (twice that of industrial practice and with an overall inlet composition well inside the flammability limits) was possible, while still achieving virtually isothermal reactor operation.

3.2.2. Catalyst development

The examples presented in the previous section clearly demonstrate the potentials of the MAFBR for partial oxidation reactions, especially to improve the selectivity, reactor throughput and safety. However, to achieve selectivity improvements by distributive dosing of air/oxygen the kinetics of the main and consecutive reactions must be such that the apparent reaction order in oxygen for the consecutive reaction is higher than for the main reaction which is often the case. Most of the consecutive reactions are active at very high temperatures and the development of newer highly active low temperature catalyst will further assist in improving the selectivity of the desired product, apart from the advantages gained by distributive feeding of oxygen. One good example is methane activation. Partial oxidation of methane and oxidative coupling of methane are carried out at very high temperatures (above 700 °C), and at these temperatures deep oxidation reactions are very likely to take place. Seeing the large reserves of the natural gas in the world and looking at the global trend towards the hydrogen economy, catalyst development for low temperature activation of methane would be of enormous benefit to the world economy. Baerns and Buyevskaya (2000) have presented an excellent review on catalytic oxidation of alkanes to olefins and oxygenates, where the development of new catalytic materials and engineering solutions have been discussed.

3.3. Miscellaneous applications of MAFB

Next to applications in heterogeneously catalyzed gas phase reactions, the use of MAFBR have been investigated for other type of applications, especially in the field of bio-reactors. Membrane bioreactor (MBR) technology is advancing rapidly around the world, both in the direction of academic research and commercial applications. Despite the increasing number of studies and full scale applications of the MBR system, direction and trends in academic research and commercial development need to be analysed. Very recently Yang et al. (2006) have critically characterized and reviewed the academic research in the area of MBRs, however no examples of applications of the fluidized bed membrane reactors have been presented. This section aims at reviewing academic research in the area of applications of membrane assisted fluidized beds as bio-reactors.

Use of a fluidized bed to promote turbulence in tubular membrane systems dates back to 1977 (Van der Waal et al., 1977). The authors used a fluidized bed to suppress the concentration of polarization in tubular membrane modules for hyperfiltration and ultrafiltration processes. This study showed that proper size of the particles is essential to avoid membrane damage by the fluidizing particles. Hoerner and Irmer (1989) used fluidized bed membrane technology using hydro-

gen as an electron-donor for the autotrophic biological denitrification. They demonstrated that membrane fluidized bed technology combines the advantages of the fluidized bed in excluding any clogging and achieving an optimal bubble free gas intake through the membranes. Because of the even gas distribution in the entire fluidized bed, the volumetric H₂ and CO₂ concentration and pH were constant and the micro-organisms enjoyed optimal conditions in the entire reactor, thereby achieving very high specific nitrate reaction rates. Jandel (1991) developed a new aeration system for fluidized bed bioreactors. Silicone membranes integrated in the fluidized bed allowed a bubble free aeration of immobilized cell systems. Oxygen was transferred by diffusion into the culture medium and delivered directly to the cells which eliminated the restriction on cell growth and productivity, as usually encountered because of insufficient oxygen supply. Hambach et al. (1992) realized a fluidized bed cell culture reactor with an integrated membrane system for bubble free oxygen supply. The effects of the system on the cellular metabolism were evaluated and possible effects resulting from the new aeration concept on fluidization properties and appropriate oxygen supply were investigated. Subsequently, Hambach (1994) used MAFBRs in cell culture technology. The mammalian cell culture was studied in a membrane fluidized bed with the focus on oxygen transport and suitability of membrane aeration in a fluidized bed. Optimization of the reactor performance was carried out. Born et al. (1997) studied the oxygen transfer via the membranes into immobilized animal cells in a membrane aerated fluidized bed, since for high cell density animal cell cultures, oxygen is often the limiting substrate. In the fluidized bed reactor the oxygen for the cells immobilized on SIRAN carriers was introduced by silicone membranes located inside the fluidized bed. The oxygen mass transfer to the immobilized cell culture has been measured to provide a guideline for the reactor design. Horner (1999) presented the technological concept for nitrate removal for the Wurzen waterworks (Germany) and showed the operating results. The waterworks used the Berko-MFT-process, an autotrophic biological denitrification applying the membrane fluidized bed technology (MFT). Detailed flowcharts of the plant were given and cost aspects were also discussed. Chaalal and Islam (2001) proposed a MAFBR as a part of a process to remove strontium cations from aqueous solutions such as those generated by nuclear reactors. The proposed scheme uses *Chlorella vulgaris* in a packed column, followed by fluidized bed membrane reactor with bentonite powder in suspension. The membrane was primarily used to keep the bentonite powder inside the reactor. However, the same system could be used to remove an additional amount of contaminant from the aqueous stream. Byong-Hee et al. (2003) used porous carriers in a fluidized bed for microbial immobilization in order to simultaneously remove organic carbon and nitrogen in wastewater. In particular, multifunctional microbial reactions in the carrier, such as simultaneous nitrification/denitrification, play an important role in the nitrogen removal. To enhance these reactions the substrates should be supplied into the carrier with appropriate rates, because the denitrification reaction rate is often limited by the supply of organic substances due to the

overgrowth of heterotrophs in the region near the carrier surface. A porous carrier–membrane hybrid process was found to have improved nitrogen removal efficiency due to stimulated denitrification as well as nitrification. Li et al. (2004) integrated ultrafiltration (UF) inside a fluidized bed pellet reactor for hardness removal. The results showed that an UF membrane alone was not effective for removing hardness due to the slow reaction kinetics of the calcium carbonate precipitation in the absence of fluidized pellets. The removal efficiency of the integrated process was 60% as compared to 16% of UF alone. Hardness removal efficiency improved with increasing pH and pellet surface area and no significant membrane fouling was observed.

4. Gas mixing in MAFBR

Fluidized beds employing fine powders are finding increased application in the chemical and petrochemical industry because of their excellent mass and heat transfer characteristics. However, in fluidized bed chemical reactors axial gas back mixing can strongly decrease the conversion and selectivity. Moreover a large part of the gas flows in the form of bubbles through the fluidized bed, which might cause reactant bypass due to bubble-to-emulsion mass transfer limitations. By the insertion of membranes in fluidized beds large improvements in conversion and selectivity can be achieved, firstly by optimizing axial concentration profiles via distributive feeding of one of the reactants or via selective withdrawal of one of the products, and secondly, by decreasing the effective axial dispersion via compartmentalization of the fluidized bed. Moreover, insertion of membrane bundles in a suitable configuration impedes bubble growth and development of macroscopic circulation patterns in the fluidized bed, thereby reducing reactant by-pass via rapidly rising large bubbles.

To assess the influence of the presence of the membrane and the permeation of gas through the membranes inside the MAFBR, the extent of gas back mixing was studied experimentally by Deshmukh (2004). Using steady state tracer gas injection experiments and ultrasound technique to measure the residence time distribution (RTD), the extent of gas back mixing was measured for fluidized beds with and without internals (membranes) in different membrane bundle configurations, viz. horizontally and vertically positioned membranes, with and without addition of gas via the membranes over a wide fluidization velocity range (Deshmukh, 2004; Deshmukh et al., 2005a,b,c).

The experimental results have clearly shown that for a fluidized bed with vertical and horizontal internals the axial gas back mixing is strongly reduced compared to a bed without internals, simply due to the presence of the internals, which obstruct the lateral movement of the bubbles by preventing bubble growth. Thus, the formation of macroscopic circulation patterns, as observed for the bed without internals is impeded (see Fig. 7a).

The addition of gas via the membranes in the bed with horizontal membranes reduced the gas back mixing enormously, even much more than due to the presence of internals. The

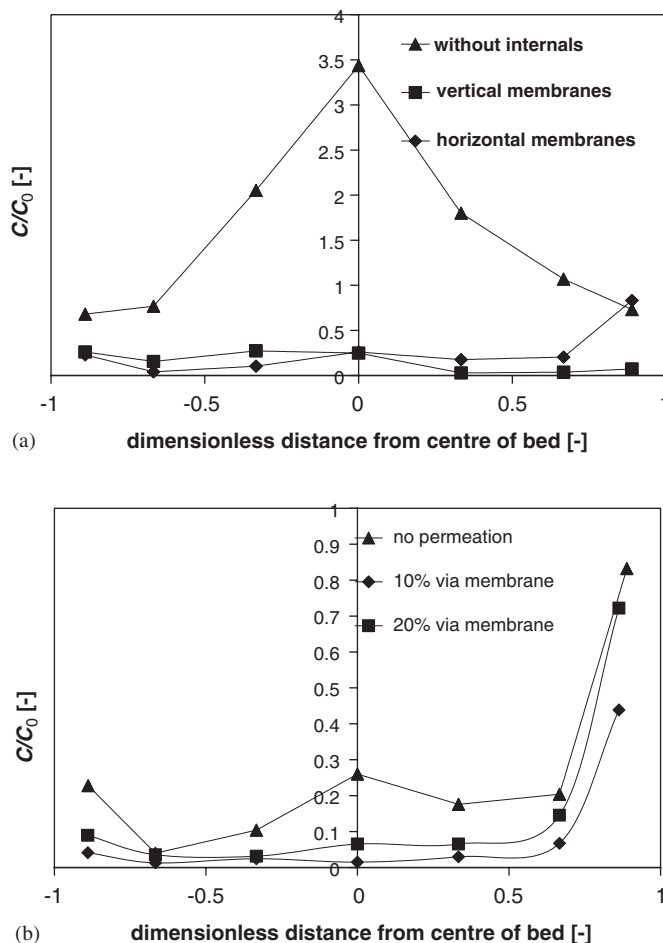


Fig. 7. Effect of (a) membrane bundle configuration and (b) gas addition via the membranes on the experimentally measured lateral relative tracer gas concentration profile (C_0 represents the completely mixed freeboard concentration) at a probe located 0.04 m from the distributor with the tracer gas injection point located at the centre of the bed and 0.16 m above the distributor for a superficial gas velocity of $8u_{mf}$ (from Deshmukh, 2004).

membrane permeation effectively annihilates the macro-scale circulation in the fluidized bed (see Fig. 7b).

Furthermore, experiments with tracer gas injected via the membranes highlighted the importance of mass transfer limitations between the bubble phase and emulsion phase. The higher the permeation through the membranes, the smaller the average bubble size and bubble fraction, hence mass transfer limitations are reduced.

5. Thermal effects in MAFBR

Fluidized beds are known for their excellent heat transfer characteristics. Isothermal reactor operation can be obtained in very large reactors as high as 10 m (Miracca and Capone, 2001). Deshmukh et al. (2005a,b,c) have demonstrated that their lab scale membrane assisted fluidized bed reactor for oxidative dehydrogenation of methanol operated virtually isothermally even for very high methanol feed concentrations (20%), while simultaneously avoiding the formation of explosive mixtures.

Furthermore, Adris et al. (1994c) addressed the issue of thermal uniformity in a fluidized bed for the highly endothermic methane steam reforming reaction system. They observed that at a gas velocity of about 5 times the minimum fluidization velocity the catalyst bed temperature became fairly uniform. Hence catalysts and membranes immersed in a fluidized bed operated above this velocity will experience virtually isothermal conditions, which results in uniform reaction rates and higher product selectivity. Packed bed membrane reactors are devoid of this feature because of axial and radial temperature as well as concentration gradients (Kuerten et al., 2004; Tiemersma et al., 2005, 2006).

5.1. Tube-to-bed heat transfer

Deshmukh et al. (2005a,b,c) experimentally investigated the effect of the presence of and the gas permeation through horizontally submerged ceramic membrane tubes in a fluidized bed on the time averaged local tube-to-bed heat transfer coefficient. They observed that the presence of membranes and heat transfer tubes decreases the heat transfer coefficient due to the reduced mobility of the emulsion phase caused by the internals obstructing the macro-scale movement of the emulsion phase, and by the enhanced bubble breakage decreasing the bubble rise velocity. Nevertheless, the measured values for the heat transfer coefficient remain reasonably high.

At high gas permeation rates through the membranes the decrease in the heat transfer coefficient at the top of the tube bundle was even stronger at high superficial gas velocities, caused by the increased bubble hold-up and/or dilution of the emulsion phase, which increases the gas film thickness over the heat transfer surface increasing the resistance to tube-to-bed heat transfer. However, lower in the tube bundle, i.e. lower in the bed, the decrease in the heat transfer coefficient was less pronounced, since these tubes experienced only part of the total gas fed via membranes. Hence, in a membrane assisted fluidized bed the product selectivity and/or operational safety can be enhanced, but care must be taken to include the effect of gas addition through the membranes on the required heat transfer surface area. Fig. 8 shows the contour plots of tube-to-bed heat transfer measured by Deshmukh (2004) at various fractions of the gas permeated via the membrane for a fluidization velocity of $6u_{mf}$.

5.2. Heat integration and autothermal operation

Apart from the integration of reaction and product separation or distributive feeding via membranes, heat integration inside the fluidized bed membrane reactor to reduce the energy consumption of the process is also of considerable interest. An initial study was undertaken by Roy et al. (1999) and demonstrated that oxygen could be introduced directly to a fluidized bed reformer to provide all of the required energy for the endothermic reforming reactions via partial oxidation and achieve overall autothermal operation. The methane conversion increased with increasing reactor temperature, oxygen

input flow rate and steam–methane ratio and decreased with increasing reactor pressure as expected. The measured methane conversion and hydrogen yield were compared to those expected at equilibrium. Full conversion of oxygen was observed for all conditions. The hydrogen yield increased with increasing temperature and steam–methane ratio. The hydrogen yield decreased minimally with increasing reactor pressure and oxygen flow rate. Subsequently, Grace et al. (2001) extended the study on the addition of oxygen for autothermal methane–steam reforming in a fluidized bed membrane reactor. They adapted an equilibrium model devised for gasification to predict the influence of various process parameters in the fluidized bed membrane reactor and showed that it should be possible to operate autothermally and free of coke formation over a considerable range of temperature, pressure and steam-to-methane ratio. In another study, Abba et al. (2002) adapted a generalized fluidized bed reactor model developed to describe a fluidized bed membrane reactor process for autothermal steam reforming of methane in a large scale unit (16 m high and 2 m wide) described by Adris and Grace (1997). This approach allowed flow regimes beyond the bubbling regime to be modelled and facilitated the treatment of the impacts of changes in volumetric flow rate due to variations in molar flow rate, temperature, and hydrostatic pressure. Improvement in the reactor performance was shown after consideration of these changes. The simulation results showed that an ultra thin membrane coating could result in reversal of the hydrogen diffusion with height, especially at elevated temperatures. The influences on the reactor performance of several other parameters such as the superficial gas velocity and steam-to-carbon ratio were also examined. It was concluded that with appropriate combinations of key operating parameters such as the methane-to-oxygen ratio, feed temperature and reactor temperature, the reactor can be operated autothermally. Recently, Rakib and Alhumaizi (2005) mathematically investigated a bubbling fluidized bed membrane reactor for autothermal steam reforming of methane with permselective Pd membranes. The oxygen fed into the reaction system could decrease the endothermicity of the overall reaction by combustion of methane, thereby reducing the need of external firing. Operation at low feed steam–carbon ratios was also possible with the steam required for the reforming reaction being provided as a product from the combustion reactions, although problems related to coking also need to be addressed at very low steam–carbon ratios. They concluded that in situ-generation of heat by the combustion reactions was a more effective means to get a better reactor performance, and a higher feed temperature could be used to supplement this performance. However, higher oxygen–methane ratios also tend to consume more of the methane itself, thus an optimum ratio exists for optimal production of pure hydrogen.

5.2.1. Multifunctionality by multiple membranes

The requirement of a high temperature for the partial oxidation of methane was effectively utilized by some researchers by applying oxygen selective dense membranes in the fluidized bed membrane reactors in order to supply the oxygen for

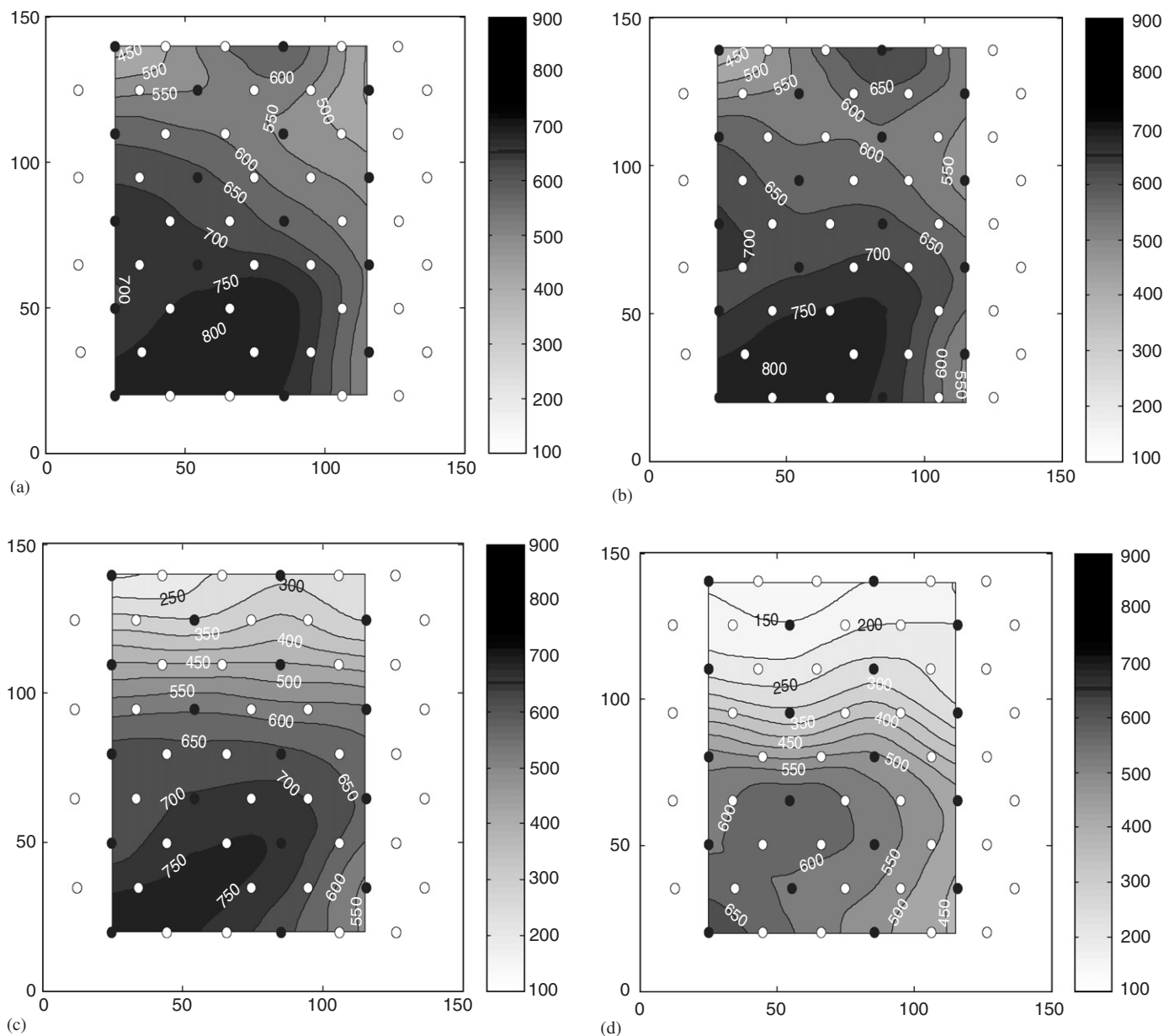


Fig. 8. Heat transfer coefficients (in $\text{W m}^{-2} \text{K}^{-1}$) of the bed at various positions in the bed at $6u_{mf}$ (a) 10% permeation; (b) no permeation; (c) 20% permeation; (d) 40% permeation. ●: Heating tube, ○: Membrane tube (Deshmukh, 2004; Deshmukh et al., 2005a,b,c).

overall autothermal steam reforming of methane, where hydrogen perm-selective palladium membranes are used to shift the reforming reaction equilibrium to completion. Two main groups are actively involved in this novel reactor technology: Kuipers group and Elnashaie group. The achievements of both groups based on these novel bi-membrane concepts are summarized below.

Chen et al. (2003) investigated the coupling of steam reforming and oxidative reforming of methane for efficient production of hydrogen over a Ni/Al₂O₃ catalyst in a novel circulating fast fluidized bed membrane reformer (CFFBMR) using a rigorous mathematical model (see Fig. 9). Palladium membranes were used for hydrogen removal and oxygen was introduced into the adiabatic CFFBMR for oxidative reforming

by oxygen fed via dense perovskite oxygen membranes. The simulations showed that high productivity of hydrogen could be obtained in the CFFBMR. The combination of these two different processes not only enhanced the hydrogen productivity but also saved the energy due to the exothermicity of the oxidative reforming. Based on the preliminary investigations, four parameters, namely the number of hydrogen membranes, number of oxygen membranes, direct oxygen feed rate and steam-to-carbon feed ratio, were carefully chosen as main variables for process optimization. The optimization study showed that the hydrogen productivity (moles of hydrogen produced per hour per m³ of reactor) in the novel CFFBMR was about 8.2 times higher than that in typical industrial fixed-bed steam reformers.

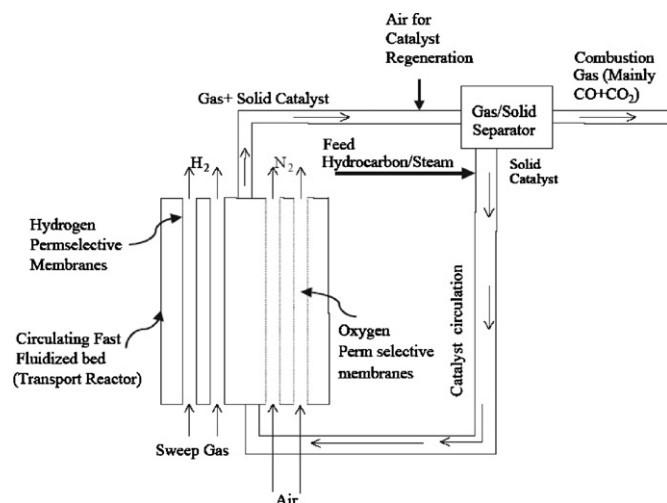


Fig. 9. Process diagram of the novel suggested CFFBMR. Reprinted from Chem. Eng. Sci., Vol. 58, Chen et al., 4335–4349, Copyright (2003), with permission from Elsevier.

Patil et al. (2005) and Kuipers et al. (2004) developed a novel multifunctional reactor concept for the production of ultrapure H_2 (< 10 ppm CO) from light hydrocarbons such as CH_4 , for online use in downstream polymer electrolyte membrane fuel cells for small-scale applications (typically < 200 kW) (see Fig. 10). A high degree of process intensification was achieved by integrating perm-selective Pd metallic membranes for H_2 removal (500–600 °C operating temperature) inside a fluidized bed reactor along with selective O_2 addition through dense perovskite membranes (900–1000 °C operating temperature). The MAFBR consisted of a partial oxidation bottom section and a steam reforming/water gas shift top section. Incorporation of both types of membranes within a single reactor had the clear advantage of producing ultra pure H_2 and pure CO_2 , circumventing expensive CO_2 sequestration. Using thermodynamic equilibrium calculations and more detailed fluidized bed membrane reactor model simulations, it was demonstrated that autothermal operation with high CH_4 conversions and H_2 yields could be achieved with a relatively small catalyst inventory. Moreover, by tuning the feed ratios to the bottom and top sections, the temperatures in both sections could be effectively controlled for optimal membrane performance.

6. Reactor modelling

The most common phenomenological description of the prevailing flow phenomena in fluidized bed reactors is based on the two-phase model of Kunii and Levenspiel (1991) and the bubble assemblage model, originally proposed by Kato and Wen (1969). The Kunii and Levenspiel model assumes that the emulsion phase is well mixed phase and the bubble phase flows in a plug flow through the emulsion phase. Mass exchange between the bubble phase and emulsion phase is accounted for by assuming a constant average bubble diameter. In the Kato and Wen model, the fluidized bed is divided in the axial direction into a number of continuously ideally stirred tank reac-

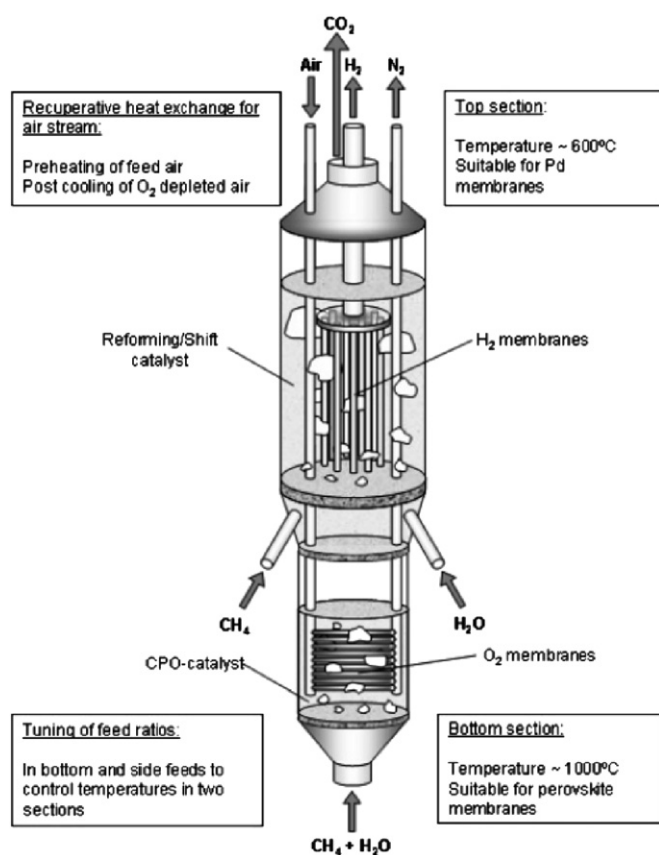


Fig. 10. Schematic of the novel fluidized bed bimembrane reactor. Reprinted from Ind. & Eng. Chem. Res., Vol. 12, Patil et al., Copyright (2005), with permission from American Chemical Society.

tors (CISTRs) for the bubble phase as well as for the emulsion phase, where the size of the CISTRs was related to the local bubble size. Both these approaches have been used to model MAFBRs. Adris and Grace (1997) proposed a model for the methane–steam reforming, which treated the fluidized bed as a two phase bubbling bed extended with gas extraction via the membranes (see Fig. 11). The model was shown to give excellent agreement with their experimental data. This model was later extended by Islam (1997), Roy (1998) and Rakib and Alhumaizi (2005) for autothermal steam reforming where oxygen was introduced to the fluidized bed with perm-selective membranes and to account for the significantly enhanced permeation of the hydrogen through the coated and more permeable membrane tubes. Subsequently, Grace et al. (2001) used the equilibrium approach to model the MAFBR for steam reforming of methane with oxygen addition. Their argument was that, when the catalyst is sufficiently active, the local concentration on the reactor side approaches close to that would be achieved at equilibrium and it is justifiable to consider chemical equilibrium as an excellent approximation for modelling the overall composition of the product stream for a given permeate flow rate. Abashar (2004) modelled a freely bubbling MAFBR for coupling of steam and dry reforming of methane. However, the derivation of the model was based on the two-phase bubbling bed reactor model of Grace (1984) the with

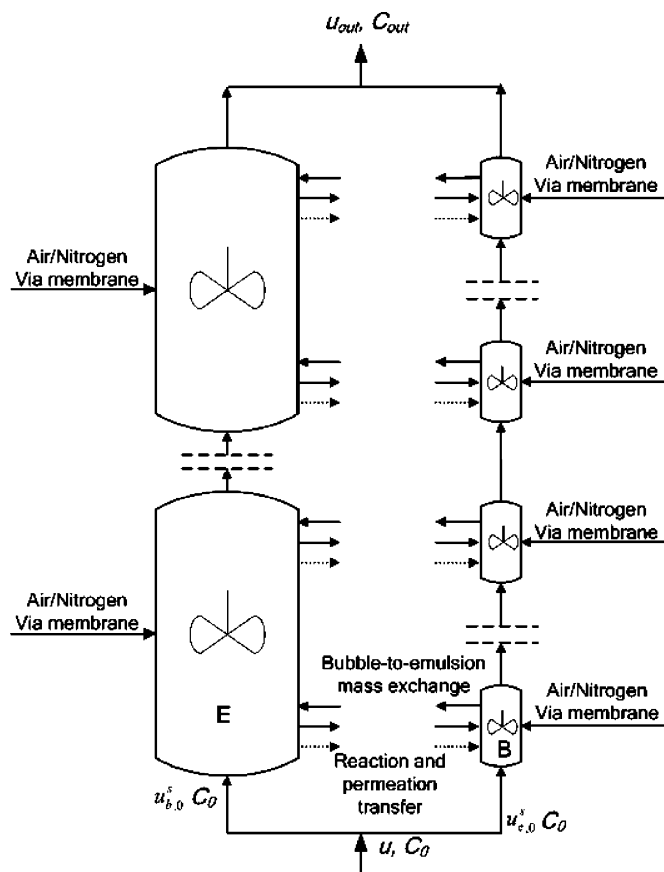


Fig. 14. Schematic representation of two-phase reactor model by Deshmukh et al. (2005); B = bubble phase, E = emulsion phase. Reprinted from Ind. & Eng. Chem. Res., Vol. 44, No. 16. Deshmukh et al., 5966–5976, Copyright (2005), with permission from American Chemical Society.

their model the fluidized bed is also divided into a number of CISTRs, however, the number of CISTRs, assumed to be of equal volume for each phase, is no longer directly related to the local bubble size, but to the extent of gas back-mixing in the MAFBR in each phase, which should be measured with independent tracer injection experiments (see Fig. 14).

These modelling studies have shown that with phenomenological two-phase models a good description of the MAFBR can be achieved, provided that good closures for the bed hydrodynamics and reaction kinetics are available. With more fundamental models validated with more detailed non-invasive experimental techniques, such as PIV (particle image velocimetry), a better fundamental understanding resulting in better constitutive equations can be obtained for the influence of the presence of the membranes and gas permeation through the membranes on the bed hydrodynamics, viz. bubble-to-emulsion phase mass transfer rate and extent of gas back-mixing.

7. Assessment of fluidized bed membrane reactors

Despite the growing number of research publications in the field of catalytic inorganic membrane reactors, very few or hardly any report on actual industrial commercialization of membrane reactors. The main reason behind this may be that in-

deed large benefits may be achieved by various catalytic membrane reactor concepts, but technological difficulties and unfavorable economics have so far prevented them from being successfully commercialized. Several research groups have attempted to summarize the problems (both practical and commercial) faced by catalytic membrane reactor technology and are very well presented in a recent review by Dixon (2003). This section summarizes the practical and commercial hurdles faced by fluidized bed membrane reactor technology identified by various research groups.

7.1. Practical and commercial hurdles

Adris and Grace (1997) examined a fluidized bed membrane reactor from scale-up and a practical point of view. They used mathematical modelling to explore potential configurations for commercial FBMR steam–methane reforming (SMR) as well as to quantify the effects of key design parameters such as membrane capacity for hydrogen removal, distribution of membrane surface area between the dense phase and the dilute phase, permeate side pressure and sweep gas flow rate. Key factors affecting the performance of a commercial FBMR were analysed and qualitatively compared with corresponding factors in packed bed membrane reactors. Issues which pose challenges to the commercial viability of this technology were identified, which included maintenance of bed mobility in case of gas withdrawal, providing sufficient membrane capacity, wear, and mechanical forces on vertical surfaces.

The principal factors affecting the performance of the membranes in a fluidized bed membrane reactor were discussed and presented. Each of the factors influencing membrane performance was discussed from two perspectives: (i) impact on membrane permeation capacity utilization and (ii) impact on membrane longevity.

7.1.1. Effect of temperature profile

The operating temperature profile to which a membrane surface is exposed is critically important for the performance of a membrane. First, due to the delicate nature of membrane construction based on dense metallic materials, strong temperature gradients can create thermal stresses, which, in turn, can compromise the mechanical integrity and hence the separation characteristics of the membrane element. A membrane surface submerged in a fluidized bed experiences a virtually uniform temperature over a wide range of superficial gas velocities (see Adris et al., 1994c; Deshmukh et al., 2005a,b,c and Patil et al., 2005). It is important to note that the permeation process is highly temperature dependent, with the permeation rate constant following Arrhenius behaviour. Therefore, a higher operating temperature should lead to a higher permeation rate. On the other hand, too high a temperature shortens the membrane life. For practical cases there should be an optimum operating temperature that gives a desirable permeation rate without unduly compromising the life time of the membrane. The optimum temperature is determined by the economics of the membrane installation and is different for each application,

depending on the type of reaction, its kinetics, and the permeation capacity requirement.

7.1.2. Efficiency of perm-selective membranes in a fluidized bed

For selective removal of one of the products from the MAFBR, the permeation rate of a desired component (e.g. hydrogen) is favoured by a high partial pressure or concentration of this component at the reaction side and a low pressure or concentration at the retentate side. In fluidized bed reactors the efficiency of the perm-selective membranes might be seriously compromised by bubble-to-emulsion phase mass transfer limitations. Most of the conversion tends to take place in the dense phase, so that reactant concentrations tend to be lower there (and product concentrations higher) than in the bubble phase. Since the surface of a membrane immersed in the fluidized catalyst bed is exposed to both phases, the driving force for the permeation process across the membrane varies from the distributor level up to the surface of the catalyst bed. The concentration profile depends on the mass exchange rates between the phases as well as on the bubble volume fraction. Both are functions of superficial gas velocity and of the bubble coalescence and splitting rates. The net permeation rate out of a fluidized bed membrane reactor system is thus affected by both the bubble and dense phases. The efficiency of the membrane performance due to bubble by-passing, and possibly due to other effects such as an additional resistance caused by a dust layer deposited on the membrane surface, can reduce the membrane capacity for hydrogen separation by as much as 60% (Adris et al., 1994c). On the other hand, the two-phase nature of the fluidized bed can also influence the efficiency (i.e., the net permeation rate) of dense oxygen perm-selective membranes, where the oxygen chemical potential gradient across the membrane is responsible for the oxygen flux into the reactor. Again, most of the conversion typically takes place in the dense phase, causing the oxygen concentration to be lowest in the dense phase, thereby strongly enhancing the oxygen permeation rate. However, no studies have yet been conducted with perovskite membranes in fluidized bed reactors. Finally, for the case of distributive feeding of one of reactants to improve the selectivity of the desired product, membranes need not necessarily be perm-selective and the efficiency of the membranes is independent of the concentration profile inside the fluidized bed. It is assumed that the gas fed via the membranes is transferred to both the phases according to their respective fractions and finally the degassing of the emulsion phase takes place as the gas is transferred to the bubble phase (Deshmukh et al., 2005a,b,c).

7.1.3. Construction and mechanical aspects

In addition to thermal stresses and the total pressure difference between the retentate and permeate side of the membrane, a number of mechanical factors can affect the performance and longevity of the membranes. In order to address the mechanical forces acting on membrane surfaces in the reactor, it is useful to first treat the construction features of membranes in each con-

figuration. Fluidized beds are known to present quite different and harsher mechanical environments in comparison to packed beds. The vigorous particle motion induced by the gas bubbles in the bed is responsible for the harsh mechanical conditions in fluidized bed systems. The buffeting action by the bubble and tube wear caused by the solid particles affect the longevity of the tube internals. A number of studies have been carried out to study these mechanical forces acting on tube internals in different orientations. While there has been considerable work on transient forces (Kennedy et al., 1981; Turner and Irving, 1982; Grace and Hosny, 1985; Pell, 1990) and wear (Zhu et al., 1990, 1991) with respect to horizontal tubes in bubbling fluidized beds, very little has been done with respect to vertical tubes. It is essential to maintain a separation distance between interior surfaces (e.g., between adjacent tubes or between the outer wall and nearest tubes) of about 30 mean particle diameters or more to avoid bridging and sticking of the particles leading to local defluidization (Grace and Harrison, 1968). Violating this condition is likely to lead to local temperature gradients and a serious loss of reactor effectiveness. This condition sets a limit on the number of tubes or other surfaces which can be inserted into a given cross section of bed. However, since very small particles can be applied in fluidized bed (typically $> 50 \mu\text{m}$), still a very high specific membrane surface area can be installed inside the fluidized bed. Alternatively, Adris and Grace (1997) suggested that tubes could be bundled together in an exterior sheath to overcome this limitation, while also helping to protect the thin-walled permeable tubes from lateral forces, wear, and plugging by particles. Next to the restriction on the inter-tube spacing to avoid defluidization, also other influences of the tubes on bed hydrodynamics and heat transfer need to be taken into account (Grace and Harrison, 1968; Harrison and Grace, 1971; Yates et al., 1984; Deshmukh, 2004). When the bubbles grow to a size larger than the distance between the immersed surfaces, the voids tend to act like slugs between the fixed surfaces. However, for tubes much smaller in diameter than the average bubble diameter, which is bound to be the case for single tubes, the bubbles tend to envelope the tubes, causing the bubbles to elongate, rise more quickly than they would otherwise, and be less likely to be diverted horizontally in pursuit of other bubbles. Hence, the tubes can be beneficial to the overall bed hydrodynamics, provided that the spacing constraints are satisfied (Adris and Grace, 1997; Deshmukh et al., 2004, 2005a,b,c). Membranes can also be arranged in the horizontal arrangement, as often encountered for heat transfer tubes. The horizontal configuration might be beneficial in case a sweep gas is used. In the bubbling regime horizontal tubes are subjected to strong buffeting forces due to the passage of bubbles and pressure waves arriving from the bed surface. Also the horizontal tube assemblies reduce the bubble size and promote a more uniform distribution of the bubble size in the tube bundle, thereby reducing the aforementioned forces on these tubes. Previous work (Yates and Ruiz-Martinez, 1987) has shown that bubbles that are large relative to the separation distance between the rows can rise unbroken through the tube bundle by bridging across. It has been observed (Ruiz-Martinez, 1988) that bubble-bridging ceases when the distance between the rows

is greater than the equivalent bubble diameter. Moreover, heat transfer from both the horizontal and vertical tube configurations is comparable. Also the horizontal tubes will have to bear the weight of the solids under bed stationary conditions. On the other hand construction of long vertical membranes might pose technical difficulties. Hence, both the configurations have their pros and cons and a choice must be made judiciously for each separate case.

7.2. Reactor design guidelines

7.2.1. Product removal via membranes

The FBMR reactor still poses research questions that have received little attention at best in the extensive literature on fluidized beds. First, the withdrawal of gas through the permeable surfaces could lead to local defluidization in the vicinity of the surfaces. When hydrogen is being withdrawn through permeable tubes in reforming or dehydrogenation reactors, the partial pressure of the diffusing species, and hence the withdrawal rate, will be highest in the dense phase (where the reaction is most rapid), and this is likely to promote local defluidization. On the other hand, counteracting this effect, in many of these processes, the total number of moles increase as the reaction proceeds, with most of the reaction (and hence production) occurring in the dense phase. Hydrodynamic studies (Adris et al., 1994a,b,c) indicate that at least some of the resulting extra moles are transferred to the bubble phase. Vertical or horizontal tubes inserted into fluidized beds can have a profound influence on bed hydrodynamics and gas mixing as studied by Deshmukh (2004). For the application of product removal, the membranes can be conveniently placed vertically in the reactor without constructional difficulty. While designing the membrane tube arrangement and its spacing, the aforementioned effects should be taken into account to avoid local defluidization and detrimental growth of the bubbles which would otherwise diminish the advantages gained by the presence of selective membranes.

7.2.2. Reactant addition via membranes

Many researchers (Deshmukh et al., 2005a,b,c; Ahchieva et al., 2005; Zhang et al., 2005a,b; Chen and Elnashaie, 2005a,b,c) have successfully demonstrated the application of membranes for the addition of a reactant into the membrane assisted fluidized bed. Most of these studies focussed on partial oxidation reactions. Deshmukh et al. (2005a,b,c) used microporous hollow fibre ceramic membranes, while Ahchieva et al. (2005) used microporous stainless steel membranes, whereas Zhang et al. (2005a,b) and Chen and Elnashaie (2005a,b,c) used dense oxygen selective perovskite membranes.

For the application of distributive feeding of one of the reactants, vertical as well as horizontal membrane configurations are possible. However, using horizontal membranes, especially for the application of controlled dosing of one of the reactants gives an additional degree of freedom in creating an axial concentration profile imposed by varying the axial reactant flow rate via the membranes. Moreover, by insertion of

horizontal membranes in fluidized beds large improvements in conversion and selectivity can be achieved, firstly by optimizing axial concentration profiles via distributive feeding of one of the reactants, and secondly, by decreasing the effective axial dispersion via compartmentalization of the fluidized bed. Furthermore, insertion of membrane bundles impedes bubble growth, thereby reducing reactant by-pass via rapidly rising large bubbles. Often cooling or heating tubes are also submerged in the fluidized bed to withdraw or add thermal energy. The effective heat transfer coefficient between the surface of these tubes and the fluidized bed is an important parameter in the design of these fluidized beds. The integrated gas addition via the membranes inside the fluidized bed strongly influences the bed hydrodynamics and thus the tube-to-bed heat transfer (Deshmukh, 2004). Therefore, there has to be an optimum in the amount of reactant that can be fed via the membranes into the fluidized bed, because when a large fraction of the total fluidizing gas is fed via the membranes, lower gas flow rates are fed via the distributor which may decrease the macro-scale movement of solids and reduce the heat transfer rates in the fluidized bed. Moreover, distributing the reactant only via the membrane will result in inefficient fluidized bed reactor because most of the reaction in the fluidized bed takes place in the bottommost part of the bed and the resistance to mass transfer from the bubble phase to the emulsion would be maximum in the top section of the bed (Deshmukh et al., 2005a,b,c).

The main problems for MAFBR include complexity in construction, scale-up and economics. It should have low costs, low risks, an available market and immediate benefits. We will need many breakthrough applications, to justify the cost of membrane development and manufacture. For example, the use of palladium membranes for hydrogen removal is not justified economically, as several studies have shown, except maybe to provide clean hydrogen for fuel cells. Oxygen permeable membranes are considered high-cost and high-risk; of the current research areas, syngas may be commercially viable. Moreover, ceramic and metallic membrane tubes have to be housed within a reactor assembly with feed/product lines and other reactor peripherals. Progress is still needed in developing cheap, high-temperature sealing systems for membrane reactors. To address this issue, a new reactive air brazing concept has been developed by Weil et al. (2004). They discussed the details of this joining technique and illustrated its use in bonding a wide variety of materials, including alumina, lanthanum strontium cobalt ferrite, and yttria stabilized zirconia. Furthermore, there is also a need to develop technologies for heat supply/removal and temperature-control for large-scale modules of membrane assisted fluidized beds.

7.3. Economic evaluation

Different analyses of effectiveness of fluidized bed membrane reactor are possible to answer the question whether they provide any real advantage over more conventional reactors. Ultimately, economics will be the decisive factor, although very few studies have included an economic evaluation. Two exceptions are the studies of Roy (1998), who investigated the

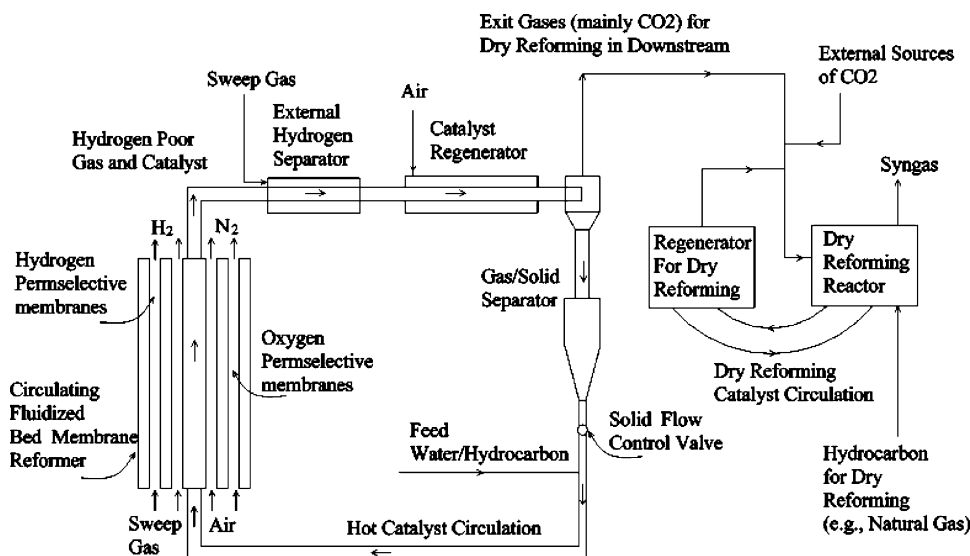


Fig. 15. Optimized autothermal reforming process for efficient pure hydrogen production. Reprinted from Ind. & Eng. Chem. Res., Vol. 44, Chen & Elnashaie, 4834–4840, Copyright (2005), with permission from American Chemical Society.

economics of the steam methane reforming reaction, and Chen and Elnashaie (2005a,b,c), who investigated the autothermal reforming of methane for hydrogen production. Roy (1998) evaluated five different plant designs with two different types of membranes. They concluded that supplying the required heat of reaction for the reforming section was the most difficult part of the process design. The primary difference between the various designs was in the method of heat transfer and in one design, a different membrane with a higher permeation flux was used. They considered capital and the operating costs in their economic evaluation. Their study identified that fluidized bed membrane reforming can have a gain of up to 35% in the methane conversion over conventional technology at comparable operating temperature and pressure. A scheme using direct fired fluidized bed reactors located in the radiant section of a reformer type furnace was considered to be the most efficient one for heat supply compared to alternative designs. The product hydrogen was ultra pure due to the very high membrane perm-selectivity. The configuration with high flux membranes had a lower capital and operating costs than conventional SMR, showing the promise of this new technology.

Chen and Elnashaie (2005a,b,c) evaluated the economics of pure hydrogen production as a clean fuel produced by autothermal steam reforming of hydrocarbons in their earlier suggested novel autothermal circulating fluidized bed membrane reformer (ACFBMR) (Chen and Elnashaie 2004a,b, 2005a,b,c). A detailed autothermal reforming pilot plant was designed, which formed the basis for the determination of the specifications and costs of the main units/equipments (see Figs. 15 and 16). Using statistical correlations and cost factors, the total capital investment was estimated. The economic analysis showed that the hydrogen production cost decreases with an increase in the plant capacity in the range of 100–100 000 kg of H₂/day. Above this region, the effect of the plant capacity becomes insignifi-

cant. For a small pilot plant with a 100 kg of H₂/day capacity, the hydrogen cost in the industrial steam methane reforming process is \$9.10/kg of H₂, while using this novel autothermal technology, the authors claimed that the costs were \$2.05/kg of H₂ assuming the methane feed and \$2.22/kg of H₂ were based on the heptane feed, thus the cost reductions of 77.5% and 75.6%, respectively. For a typical large industrial plant with 2.14×10^5 kg of H₂/day (equivalent to 10^5 Nm³ of H₂/h; Scholz, 1993), the reported industrial hydrogen production cost by steam methane reforming is \$0.74–0.97/kg of H₂, while using this autothermal technology, the hydrogen production costs were \$0.66/kg of H₂ from heptane and \$0.50/kg of H₂ from methane, respectively. The cost reductions are 10.8–32.0% and 32.4–48.5%, respectively. The comparison of hydrogen production costs over a wide range of plant capacities illustrates that this novel ACFBMR can be a much more efficient and more economical pure hydrogen producer.

7.4. Commercialization

Contrary to the packed bed membrane reactor, for which hardly any industrial commercialization was realized in last the three decades, signs are showing the beginning of the commercialization of the fluidized bed membrane reactors for the production of the pure hydrogen for fuel cell applications. The most important initiative towards commercialization is by “Membrane Reactor Technologies Ltd.”, a privately owned, Vancouver-based technology firm with activities focussed on the development and commercialization of membrane reactor systems. With the application of its patented Fluidized Bed Membrane Reactor (FBMR) technology to steam methane reforming, the company is poised to become a competitive supplier of small to medium scale, pure hydrogen production units for the industrial hydrogen market and the emerging hydrogen economy.

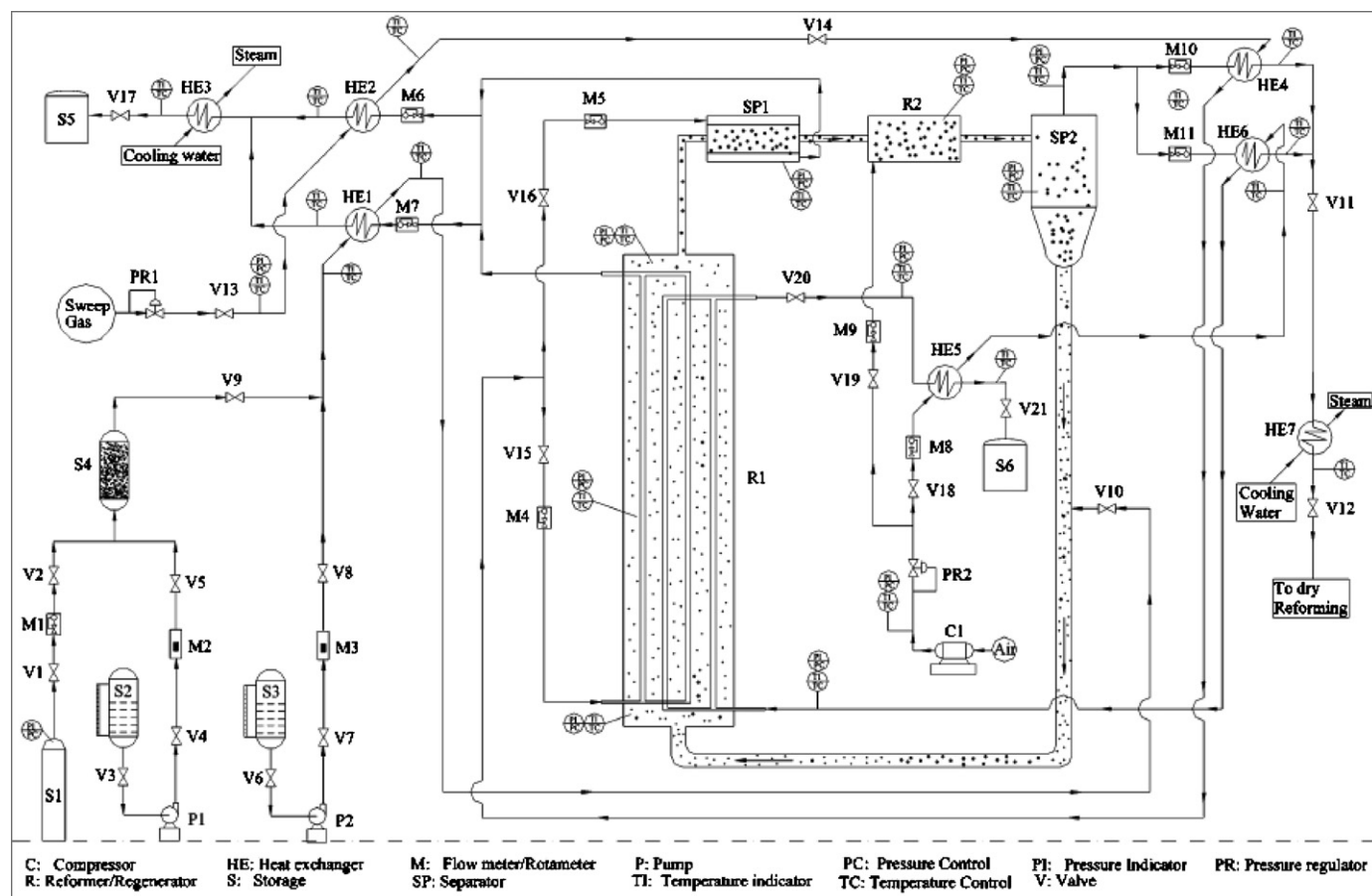


Fig. 16. Detailed pilot plant for the novel optimum autothermal reformer–regenerator process. Reprinted from *Ind. & Eng. Chem. Res.*, Vol. 44, Chen & Elnashaie, 4834–4840, Copyright (2005), with permission from American Chemical Society.

MRT's integrated hydrogen generation system includes all equipment required to convert as-supplied natural gas to pure, pressurized hydrogen. Natural gas is conditioned by sulfur removal, compression and preheating before feeding to the single step membrane reactor. A combination pre-heater, using reactor off gas as fuel, also raises the steam needed for the reforming reaction. The heart of the system is the membrane reactor where the natural gas and steam mix intimately with catalyst in a fluidized bed, ensuring optimum heat and mass transfer conditions. Perm-selective membranes within the reactor continuously withdraw pure hydrogen driving the equilibrium forward and maximizing the yield of hydrogen from the natural gas feed. Optimized internal oxidation provides additional energy to drive the reaction. Heat integration is maximized to recover energy. Compressors within the system for natural gas, air and hydrogen are selected based on the available supplies and to meet the needs of the end-user. The system is designed for automated, unattended operation with key parameters monitored and controlled and for fail-safe operation by an on-board controller. The unit is designed for compactness and ease of access and is delivered on a self-contained, enclosed skid.

8. Conclusions and recommendations

The interest in developing high temperature MAFBR is still strong, which is also reflected by the number of publications on this topic in the recent years. There is also a progress towards commercialization of the MAFBR for the selective removal of hydrogen. However, from an industrial point of view there are still many issues to be addressed before putting a case for successful commercialization, such as the costs of membranes and their stability in the harsh fluidization conditions. However, engineers are showing creativity in finding new configurations of MAFBRs for the effective utilization of available membranes. A shift in the attention is observed from circumventing equilibrium limitations by product removal via perm-selective membranes, towards selectivity increase by controlled dosing of reactants via poorly perm-selective microporous membranes. Distributed feed of oxygen, especially for partial oxidation of alkanes and alcohols is expected to be a growing research area. Attention is also being paid to the application of dense perovskite membranes for the in situ separation of oxygen from air, but currently their application is limited to the very important methane partial oxidation applications because of the very

high temperatures required to achieve acceptable oxygen permeation rates.

Also the level of sophistication in experimental as well as modelling approaches is increasing. Novel and fundamental studies on gas back mixing and tube-to-bed heat transfer in the presence of membrane and gas permeation via the membrane in the MAFBRs have been carried out. Results are certainly encouraging because of improvement in the hydrodynamic characteristics (smaller bubbles, annihilation of large scale circulation patterns, approaching plug flow conditions) while at the same time retaining good heat transfer characteristics. More detailed models are being developed for the entire range of flow regimes possible in the fluidized beds, including the effect of the presence of membranes and gas addition/removal via the membranes on the local bubble size and bubble to emulsion mass transfer rates.

It is clear that there are several areas that require additional research and clarification if FBMR reactors are to become commercially viable. Key areas requiring investigation include the magnitude of forces on vertical as well as horizontal membranes tube assemblies and the effects on the fluidization behaviour (heat transfer and bubble size distribution) of gas addition as well as withdrawal through permeable surfaces and of gas generation due to the reactions. Also the long-term durability of the membrane material under fluidization conditions, the maintenance of the permeable surface free from blockage and the optimum reactor design and sweep gas configuration need to be further investigated.

The progress that has been made till now suggests that the challenges to the commercialization of the MAFBRs will be met in the future, especially for controlled oxygen/air dosing using porous membranes for partial oxidation reactions and perm-selective hydrogen withdrawal in steam or autothermal steam reforming for ultra-pure hydrogen production.

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