EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Membrane Reactors (selective)

TECHNOLOGY CODE: 2.2.2

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1. Technology

1.1 Description of technology / working principle
(Feel free to modify/extend the short technology description below)

A membrane reactor, strictly speaking, is an apparatus combining the accomplishment of a chemical or biochemical reaction with separation through a membrane in *one device*. Yet a slightly wider definition shall be adopted here, claiming that the membrane and the reactor must *mutually affect each other's operation* (Sanchez Marcano and Tsotsis, 2002) for the combined system to qualify as a membrane reactor. This also includes separate units which are, though, connected through a recycle stream. The membrane, theoretically, is permeable only to one component (or a group of components) of the reaction mixture, i.e., it provides a *selective* separation. The use of *non-selective* membranes in chemical reactors is discussed in a separate report (technology code 1.2.7). However, some of the objectives of the use of membranes in chemical reactors apply to both types, thus a certain overlap between the two reports is unavoidable. In practice a sharp distinction between selective and non-selective membranes is often not possible anyway, i.e., certain membranes may or may not show selective transport depending on the experimental conditions (e.g., microporous membranes), and the conflict between high permeance and high selectivity, i.e., high selectivity is usually achieved at the expense of permeance, may well render a membrane with high permeance but moderate selectivity an optimal compromise in a given situation.

Due to the integration of additional functions into the reactor, membrane reactors are multifunctional reactors. Various objectives are addressed by integration of reaction with separation, which can be distinguished according to the hierarchical level they affect.

1. Process level (eliminating process units and state changes between them):

   The integration of a separation function into the reactor, which otherwise would require its own apparatus, allows to decrease the number of process units. This is especially attractive if it eliminates interstage temperature and/or pressure changes required in the conventional process scheme. However, to achieve a synergetic coupling of the two functions requires that the reaction conditions are compatible with the conditions of the membrane separation. The expected benefits are reduced footprint and complexity of the plant and hence lower investment costs. An increased efficiency additionally results in savings on energy and raw materials.

2. Reactor level (optimising the contact between the phases and the dosing strategy):

   The ability of a membrane to transport material can be exploited in a reactor in various ways to enable higher efficiency of the combined process compared to separate units. One approach is to quickly remove products from the reaction zone that have a negative influence on the kinetics. This applies, e.g., to equilibrium reactions where the reverse reaction is suppressed by removing one of the products. In a broader sense, it applies to all reactions where certain products compete with the reactants, e.g., for active sites on the catalyst; included is an inhibition by reversible adsorption, irreversible poisoning, or unwanted side reactions of the products (the reverse reaction is a special case hereof). By keeping the concentration of such products low, even at high conversion, a high reaction rate can be maintained resulting in higher conversion; eventually, the reaction can be driven to completion. As a result of an improved

reactor performance, downstream processing may become less expensive, e.g., if separation and recycling of unconverted reactants are reduced or even totally avoided. Similarly, milder reaction conditions may become applicable decreasing the energy demand and/or the standards imposed on construction materials. Another feature one might want to utilise is the possibility of implementing an advanced dosing concept such as distributed feeding of a reactant along the reactor. High selectivity of the membrane is not compelling for that purpose, e.g., if the flux through the membrane can be properly set by the differential pressure (see also technology report 1.2.7). There may be different aims of distributed feeding: one is to establish a uniform concentration profile of the dosed species along the reactor if this gives higher selectivity or yield or improved safety of the process. If suitable membranes were available, or a design in sections was feasible one could also go for a specific shape of the concentration profile, if this payed back in terms of reactor performance due to kinetic reasons. Another effect observed for distributed feeding is an increasing flow rate downstream the reactor. Together with the fact that fluid elements entering the reactor further downstream will have a reduced residence time compared to fluid elements supplied at the entrance, this severely alters the residence time distribution and may improve the yield of intermediate products in consecutive reactions. Finally, a membrane can be used to provide the reaction zone. For reactions relying on a catalyst, an active material may be incorporated into the membrane. This can be done uniformly or only in a certain region, e.g., a thin surface layer. Two reactant streams may then be passed along the different sides and mix in the catalytic zone by diffusion. One would mainly think of porous membranes and a solid active material coated on the pore walls for this kind of configuration due to the higher flux compared to dense membranes. But other types are also conceivable, e.g., a molecular catalyst dissolved in a liquid filling the pores of a support. Even if no catalyst is required, the same principle may still be applied if the reaction is sufficiently fast to reach complete conversion within the membrane.

3. Reaction level (influencing the reaction mechanism through the chemical nature of the membrane):

   With a dense membrane employed in the reactor it would be possible that the membrane, due to its chemical nature, supplies one of the reactants in a special form which is more active or selective in the reaction pursued than in its usual form. A ceramic oxygen ion-conducting membrane is an example; it is capable of passing oxygen ions to a solid catalyst attached to it, instead of using molecular oxygen from the reactant gas phase. Other examples include silver membranes, which selectively permeate atomic oxygen, or membranes made from palladium or its alloys that are permeable exclusively to hydrogen (in atomic form). Proton exchange membranes known from PEM fuel cells represent another class of membranes that may be used for such a purpose.

Most often membrane reactors involve catalysts, as most industrial reactions rely on catalysts. This brings about different options for arranging the catalyst in respect of the membrane, i.e., an inert membrane used together with a conventional catalyst (packed-bed, fluidized-bed, slurry or structured catalyst, etc.), or a catalyst intimately combined with the membrane, e.g., if the membrane surface itself is catalytically active or if the catalyst is placed into the membrane support (assuming that the membrane is a thin film on a structural support). The first category is called inert membrane catalytic reactor while the second one qualifies as an actual catalytic membrane reactor. In either case, the mass transport rate through the membrane and the rate of the reaction must be compatible in order to achieve the synergetic effects expected from the coupling of reaction and separation.

It should also be noted that fuel cells, likewise, qualify as catalytic membrane reactors, as they involve catalyzed reactions at both electrodes as well as selective transport of defined (charged) components, e.g. protons or oxygen ions, through an electrolyte membrane connecting the anode and cathode compartment. A fuel cell setup may also be operated in electrolysis mode, i.e., with external voltage applied to perform an electrochemical synthesis. Both versions, fuel cells and electrolysis cells, can be subsumed under the term electrochemical membrane reactor.

Membrane reactors have been addressed in numerous scientific publications and patents, the majority of which over the past two decades. Pioneering studies were performed already back in the 1960s in the United States (Pfefferle, 1966) and the former Soviet Union (Gryaznov, 1968, 1970, 1986) on membrane reactors with hydrogen permeable walls. Since that time the scientific production (journals and patents) in this area has risen to > 250 new publications per year (e.g., in 2005) with keywords "membran?" and "react?" in the title. Catalysts are involved in about 100 of these publications, as suggested by the presence of the additional keyword "cataly?" in the title. It is impossible to cover all developments in this report. However, many reviews on membrane reactors are available for further information (see, e.g., Dittmeyer and Caro, 2008, and the references therein).

Notwithstanding the large number of publications, commercial success of membrane reactors, as yet, is limited to few areas. Membrane bioreactors and biofilm reactors for water and wastewater treatment have enjoyed increasing commercial success over the last years due to technical innovation and significant membrane cost reduction (Judd, 2006). Enzyme membrane reactors are established in the fine chemicals industry, and the same approach of using ultrafiltration membranes for separation of high molecular weight catalysts from the crude product to enable continuous processing has been extended, more recently, to molecular weight-enlarged homogeneous catalysts, called chemzymes (Wöltinger et al. 2005). Pervaporation membrane reactors also have found first commercial applications (Lipnizki et al. 1999).

Apart from this, only small-scale industrial operation was reported for reactors with metal membranes in selective hydrogenations in the pharmaceuticals sector (see Gryaznov and Orekhova, 1998, and Sanchez Marcano and Tsotsis, 2002), pilot scale experiments were described for different applications, and there are major industry-led development projects targeting large-scale membrane reactors for hydrogen and for syngas production, while the industrial application of membrane reactors on a wider scale is yet to come.
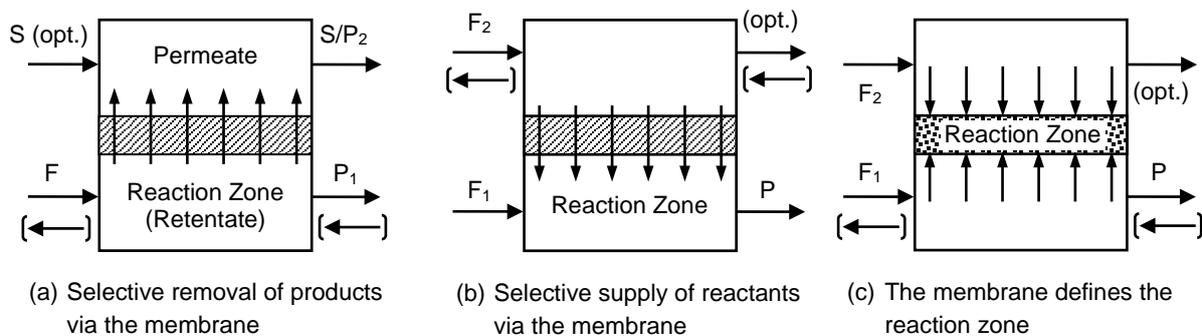
1.2 Types and "versions"
(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Membrane reactors (MR) can be classified according to functional or material aspects. The functional classification is largely independent of the membrane material and therefore more suitable to start with.

Depending on the main intention for the use of the membrane, three different types of membrane reactors are distinguished, i.e., the extractor MR (see Fig. 1a) where one of the products is selectively extracted from the reaction mixture, the distributor MR see (Fig. 1b) where the membrane distributes one of the reactants to the reaction zone, and the contactor MR (see Fig. 1c) where the membrane serves to provide a region for contacting of the reactants.

1.2.1 Extractor MR

This is the most widespread MR concept. It is mainly applied to equilibrium-restricted reactions to increase the yield of the desired products beyond the equilibrium value. Given the intention to overcome the equilibrium restriction, conversion must not be limited by the reaction kinetics; i.e., the reaction must be sufficiently fast compared to the mass transport through the membrane, a feature summarized by the term "kinetic compatibility". As stated in section 1.1, the ultimate target is to drive the reaction to completion, but for this those products not removed through the membrane must not inhibit the reaction kinetically, for example by competing with the reactants for adsorption sites. If the desired product is removed through the membrane selectively enough for the target application, then the membrane reactor not only benefits from overriding the equilibrium constraint but also provides an integrated purification which allows the number of process units to be decreased.

(a) Selective removal of products via the membrane

(b) Selective supply of reactants via the membrane

(c) The membrane defines the reaction zone

Figure 1: Different types of membrane reactors. (a) Extractor, (b) Distributor, (c) Contactor. F stands for "feed", P for "product", and S (opt.) for "sweep gas (optional)".

The transport through the membrane in an extractor MR is usually driven by the difference of the chemical potential of the permeating species between the retentate and permeate side surface of the membrane. For a gaseous phase at moderate pressure the driving force can be approximated by the partial pressure difference. Three possibilities exist to create the driving force:
   a) Use of an inert sweep gas in the permeate compartment.
   b) Application of a pressure difference between retentate and permeate compartment (retentate overpressure and/or permeate evacuation).
   c) Use of a reactive sweep gas to consume the permeated species.

Which of these options is preferred depends on the situation. In general, an inert sweep gas is not a good choice as it must be provided and compressed, and a diluted gas mixture is obtained which normally is of little use. If the reaction kinetics allows higher pressure, this becomes an attractive option because then the pressure difference is sufficiently large to drive out the permeated product. The benefits are that no sweep gas is needed and that the product is obtained in high purity. On the other hand, the feed gas must be compressed whereas the product accrues at low pressure, which limits its usability and eventually requires recompression. The third option, i.e., converting the permeated product with a reactive sweep gas, is promising as it avoids the disadvantages of the other two. Moreover, this option allows to generate or consume heat directly in the permeate compartment which greatly improves the heat transfer. The downside of coupling two reactions via one reactant or product transported through the membrane is a more difficult control of the system (e.g., temperature profiles) due to the reduced degree of freedom.

1.2.2 Distributor MR

One of the reactants is distributed through a membrane along the reaction zone. This concept has been proposed mainly for multiple reaction networks where the kinetics

(and not the thermodynamics) controls the yield of the desired product, and the rates of the undesired reactions depend more strongly on the concentration of the reactant supplied through the membrane than the rate of the target reaction. Selective oxidation of an alkane with oxygen in the gas phase is a typical example. These are exothermic reactions, for which a control of the reaction rate is important not only to preserve high selectivity but also for safety reasons. If the limiting reactant is distributed along the reactor through a membrane, its concentration profile in the reaction zone will be flat, as opposed to an exponential decay with the highest concentration at the reactor inlet in conventional mixed-feed operation. The maximum concentration (in a mixed feed) is often dictated by the explosion limit; it also determines the maximum conversion in the reactor. With separate feeding of the reactants, one being supplied at the reactor entrance and the other distributed over the length, a higher amount of substance of the limiting reactant can be fed while staying safely below the explosion limit. In turn higher conversion is expected without loss in selectivity. However, whereas this idea holds for parallel reactions where the undesired pathway has a higher kinetic order in respect of the limiting reactant, it is not *generally* applicable to consecutive reactions or parallel/consecutive reaction networks where the intermediate is the target product. This is because the rate of the subsequent reaction increases with increasing concentration of the intermediate, if not restricted by depletion of the limiting reactant. Thus, a flat concentration profile of the limiting reactant over the reactor length may significantly reduce the selectivity as conversion increases. A gradually decreasing transmembrane flux downstream the reactor might offer a solution to this problem, as it allowed fine-tuning of the concentration profile to match the demands associated with the kinetics of the actual reaction system. This might be achieved by a design in sections or by gradual variation of the membrane properties, if technically feasible.

Just as for the extractor MR, in a distributor MR a membrane capable of extracting the desired reactant selectively from a mixture with undesired components provides an additional benefit on the process level; then again, one process unit may be eliminated. Oxygen ion selective ceramic membranes for catalytic partial oxidation of hydrocarbons, e.g., fall into this category.

1.2.3 Contactor MR

The membrane is used to provide a structured space for enabling a reaction between the constituents of two separate fluid streams. The objectives of this concept include the mixing of reactive species not until the point of the reaction, an improved mass and/or heat transfer due to short transport paths, or favourable hydrodynamic conditions in the confined space inside the membrane structure. Contactor MRs are mostly associated with non-selective, e.g., porous membranes, mainly due to the higher permeance offered (see technology report 1.2.7). With a catalyst involved in a contactor MR, this can be viewed as a structured catalyst with extended functionality. If a selective membrane is used in a contactor MR, the resulting system automatically qualifies either as an extractor MR, or as a distributor MR, or as both, depending on the intention for its use. A polymer membrane used to protect an embedded solid catalyst from being poisoned by certain constituents of the reactant mixture may serve as an example (Fritsch et al., 2003, see also Dittmeyer et al., 2004).

1.2.4 Reactor Design Considerations

In addition to the mass transport function fulfilled by the membrane, MRs may be distinguished based on the reactor design, e.g., packed-bed MR, fluidized-bed MR, slurry MR, catalytic membrane module and other, more specialized designs. This extends to different options for the guiding of the retentate and the permeate flow (counter-current, co-current, cross flow).

Basically, the key points for the design of a MR are the same as for the design of a conventional reactor, e.g., the existing phases in the reactor (including an optional catalyst), the kinetics of the reaction and of the mass transport between and within

the various phases, and the heat transfer from and to the reactor and between the phases inside it. Most MR designs are, though, signifcantly more complex than conventional reactor designs, mainly due to the need (1) to integrate, additionally, a large membrane area separating two compartments within the reactor volume, (2) to provide suitable means for an effective heat and mass transfer between the membrane and the surrounding fluid phases, and (3) to allocate an appropriate membrane area per unit volume of the reactor/catalyst depending on the kinetic requirements of the coupled system of reaction and permeation. Consequently, the variability of the designs for MRs is even larger than for conventional reactors. Two extremes may be distinguished, though. If the combined process is dominated by the chemical reaction part of it, i.e., if the catalyst or the reactor volume are decisive while only a small membrane area is needed, then the design will be evocative of a conventional reactor. Conversely, if the combined process is dominated by the membrane part, i.e., the reaction is very fast, the design will look more like a typical membrane module, e.g., plate and frame, hollow fibre, or a fuel cell stack.

1.2.5 Material Aspects of the Membranes

As mentioned, the mass transport across a membrane can be selective if only one component of a mixed feed permeates through it (see Fig. 1a/b) or non-selective if all species pass through at comparable rates (see Fig. 1c). Permselective transport is found in dense membranes and is usually governed by a solution-diffusion mechanism. Common examples include metal membranes which are exclusively permeable to hydrogen, i.e., palladium, palladium alloys, group Vb metals and alloys thereof, or to oxygen, i.e., silver, ceramic mixed oxygen ion conducting or proton conducting membranes, and to some extent also dense polymer membranes. Non-selective transport normally occurs in macro- and mesoporous membranes. They are typically made from metals (macroporous membranes only), ceramics or glass, or polymers. In mesoporous membranes (pore diameter from 2 to 50 nm) Knudsen diffusion is often the dominating transport mechanism. Microporous membranes (pore diameter below 2 nm) represent a bit of both: Selective and non-selective transport is possible depending on the size of the permeating molecules compared to the pore size and on their interaction with the membrane material. Two categories of microporous membranes have to be distinguished. Membranes with pore sizes close to the kinetic diameter of the molecules are called molecular sieving membranes. Examples include MFI zeolites (silicalite-1, pore size 0.55 nm) for separation of xylenes or of n-/i-hydrocarbons, deca dodecasil 3R zeolite (pore size 0.36×0.44 nm) for separation of carbon dioxide from methane, and H-sodalite (pore size 0.28 nm) for separation of hydrogen from gas mixtures. X-ray amorphous metal oxide membranes, mainly silica, and carbon molecular sieve (CMS) membranes also belong to this class. In contrast, membranes relying on the adsorption properties of the membrane material, e.g., microporous carbon, are called selective surface flow membranes.

1.3 Potency for Process Intensification: possible benefits
(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO$_2$ emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

The potential benefits of membrane reactors depend largely on the nature of the application. It is not possible to address all interesting proposed applications of membrane reactors here. Therefore, the information provided in Table 1 refers to high-temperature catalytic membrane reactors for hydrogen production (hydrogen permeable membranes, i.e., mainly metals) or syngas generation (mixed oxygen ion and electron conducting ceramic membranes) which currently represent the two most extensively studied applications of membrane reactors worldwide.

Large-scale hydrogen production may be aimed at pre-combustion capture of carbon dioxide in electrical power generation in IGCC power plants, or at syngas preparation for bulk chemicals. Small scale hydrogen production is mainly for supply of stationary fuel cells or fuel cell vehicles (filling stations or on-board reforming) with ultrapure hydrogen, or for other local applications, e.g., in metallurgy or in the glass industry.

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	35-60% 12%	• Projected energy savings for production of H_2 or O_2 (oxy-fuel combustion) for electrical power generation in IGCC power plants • Estimated energy savings for syngas preparation for large-scale ammonia synthesis in a Pd/Ag membrane reformer
Less CO_2 emissions	75-95%	• Membrane reactors with H_2-selective membranes (pre-combustion capture) are expected to halve the efficiency penalty for CO_2 capture in electrical power generation compared to conventional gas absorption technology (post-combustion capture). Efficiency penalties of 4-5% are predicted for pre-combustion capture with membrane reactors. CO_2 emissions can be reduced by ca. 75%. • Membrane reactors with ceramic oxygen-ion transport membranes for syngas generation through partial oxidation of light hydrocarbons (e.g., natural gas) or through gasification of coal enable capture of ca. 95 % of the carbon dioxide generated, since nearly all the carbon dioxide is in the high pressure syngas rather than diluted in low pressure flue gas, as would be the case in conventional steam methane reforming
Cost savings	35-60%	• Predicted cost reduction for syngas preparation utilizing membrane reactors with metallic membranes (H_2 removal) or ceramic ion transport membranes (H_2 removal or O_2 supply, respectively). Both investment and operating costs are reduced. • Membrane reactors for pre-combustion capture of carbon dioxide are predicted to reduce the capture costs from > 50 €/ton to < 25 €/ton.
Increased yield and/or selectivity	up to 100%	• Membrane reactors may allow significantly higher yields in reversible reactions, theoretically up to 100%, by avoiding constraints imposed by the reaction equilibrium through removal of the products. The same holds for reactions that are kinetically inhibited by certain products.
Increased safety	Inherently safe process designs are possible	• Explosive mixtures are avoided in selective membrane reactors by keeping the reactants separated through the membrane.
Simplified process designs	fewer process units	• For example, in the production of ultrapure hydrogen for fuel cells by steam methane reforming, a single unit membrane reformer is able to replace the conventional steam reformer, the downstream water gas shift reactor (high temperature shift and low temperature shift), the preferential oxidation reactor, and the final hydrogen purification unit (e.g., pressure swing adsorption).

More compact plants	70 % volume reduction	• Reported by Tokyo Gas for a membrane reactor system for small-scale methane steam reforming with metallic hydrogen-permeable membranes (based on a demonstration unit with ca. 40 m_N^3/h H_2 productivity)

1.4 Stage of development

Membrane reactors with selective membranes enjoy a wide range of proposed applications which, however, have reached very different stages of development. As far as low-cost polymer membranes are concerned, for which the application temperature generally is restricted to ca. 100°C, the technology is commercially ready and has already reached commercial success in some fields. Membrane bioreactors for water and wastewater treatment represent the most advanced example.

Enzyme membrane reactors also have found commercial application, and the more recently developed chemzyme membrane reactors might also find applications in the near future. The same applies to pervaporation membrane reactors.

Among the many other proposed applications of membrane reactors, two fields targeting high-temperature catalytic membrane reactors continue to attract particularly high attention worldwide. One concerns membrane reformers for hydrogen production from natural gas, LPG, and other hydrocarbons, as well as high-temperature water gas shift membrane reactors as a component of process schemes for hydrogen production from coal or biomass by gasification or partial oxidation or in IGCC (internal gasification combined cycle) power plants.

The other area comprises high-temperature mixed oxygen ion and electron conducting ceramic membrane reactors for syngas production by partial oxidation of hydrocarbons, mainly natural gas (also combined with IGCC). Both areas, technically, are extremely challenging (membrane materials, reactor design, etc.). The development today is mainly pushed by industry-led consortia. The scientific bases have already been laid and promising materials, reactor designs, and process configurations were identified and patented. First industrial-scale pilot plants were built and are being operated to provide data for further technological development and scale-up. This also includes manufacturing lines for single membranes and modular membrane elements. Long-term stability of the systems in operation is being tested and attempts are being made to further reduce the fabrication costs. The target set for commercial readiness is within approximately 3-8 years, i.e., around 2010-2015.

Most other proposed applications of membrane reactors are either still curiosities, in the research phase, or under development in laboratory scale or, at most, in pilot scale mainly at universities and research institutes (see further).

2. Applications

2.1 Existing technology (currently used)
(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

The vast majority of chemical processes today are based on separate unit operations for performing the reaction and the required upstream and downstream separation and purification steps. Combining the reaction with separation by distillation, i.e., reactive distillation (see other technology reports), is the most remarkable exception; it may serve here as an example for a very successful combination of several unit operations into a highly integrated multifunctional unit which found widespread use in

the chemical industry. The idea of integrating a selective membrane into a chemical reactor strives for exactly the same benefits.

2.2 Known commercial applications
(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

Commercial applications of selective membrane reactors exist in the field of water and wastewater treatment (membrane bioreactors) and also in the fine chemicals industry (enzyme membrane reactor). Pervaporation (or vapour permeation) membrane reactors as well have found some industrial applications. High-temperature membrane reactors for hydrogen production through reforming of light hydrocarbons or coal gasification, each followed by water gas shift conversion are being developed in industry-led consortia in different places worldwide. The same holds for high-temperature membrane reactors for syngas generation by partial oxidation of hydrocarbons.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity / Plant size	Year of applica-tion	Reported effects
Water and wastewater treatment (for dis-charge or water re-use)	• Zenon, Canada, (ZeeWeed®) • Norit, The Netherlands, (X-Flow) • Siemens Water Technologies, Germany (former US Filter, USA) • Huber (VRM®), Germany • Koch (Puron®), USA • Kubota, Japan, (Kubota submerged membrane unit) • Mitsubishi Rayon, Japan, (Sterapore®), • Toray, Japan	Submerged polymer membranes in a bioreactor, or membrane module installed downstream a bioreactor	Capacity: 20-130.000 m^3/d (a typical flux is 0.5 m^3/m^2d, i.e., membrane area is 40-260.000 m^2)	Since ca. 1995 expo-nential increase of MBR installa-tions	Membrane fouling is the main problem and is minimised by two-phase flow regime, reduced solids content (10-15 g/l) and modest fluxes Energy input in modern MBR plants required for fouling control is ≤ 1 kWh/m^3
Fine chemicals industry	Degussa	Enzyme membrane reactor	Several hundred tons per year	1982	Production of pure L-amino acids via the acylase route
Fine chemicals industry	Degussa	Enzyme membrane reactor	Unknown	1999	Production of (S)-*tert.*-leucine and (S)-neopentyl-glycine by

| Fine chemicals industry | Chemox, India (Process commercialised by Sulzer Chemtech) | Pervaporation membrane reactor (hydrophilic membranes) | Unknown | Unknown | Acceleration of ethyl oxalate synthesis due to continuous water removal |
| Fine chemicals industry | Unknown (Process commercialised by Sulzer Chemtech) | Pervaporation membrane reactor (organophilic membranes) | 8.5 t/d | Unknown | Synthesis of a methyl ester using pervaporation for continuous extraction of methanol |

(Row above continues from previous page with: dehydrogenase technology with integrated cofactor regeneration)

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

There are several large ongoing industry-led development projects on selective membrane reactors for production of hydrogen or syngas. These efforts target local production of hydrogen, e.g., for fuel cell vehicles, cost-effective large-scale generation of syngas for production of liquid transportation fuels from natural gas, coal or biomass, and the generation of electrical power with carbon dioxide capture in integrated gasification combined cycle (IGCC) power plants; hydrogen permeable membrane reactors are employed for pre-combustion capture of carbon dioxide whereas oxygen permeable membrane reactors are used for oxy-fuel combustion. In some of these projects industrial demonstration units have been built and operated. Table 3 gives some information on these activities.

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Hydrogen production	Tokyo Gas Co. Ltd., Tokyo, Japan, with partners	Fixed-bed steam methane reformer with sinter metal supported composite Pd alloy membranes. System for local production of fuel cell grade hydrogen, operated at a filling station in Tokyo (Senju hydrogen station).	Unknown	• 40 m_N^3/h H_2 demonstration unit. • 70% reduction by volume and 50% reduction by footprint compared to conventional reforming technology with pressure swing adsorption for H_2 purification. • Stable operation for more than 3000 h. • Hydrogen purity

				• better than 99.99% • Thermal efficiency 76% • Membrane durability must be improved, cost reductions for membrane and reactor design are needed
Hydrogen production	Membrane Reactor Technologies (MRT) Ltd., Vancouver/BC, Canada, with partners - Linde Group (BOC Group Inc.) - HERA US Inc.	Fluidised-bed steam methane reformer equipped with Pd alloy membranes. Oxygen injection into the fluidized bed. Hydrogen compression by novel thermal metal hydride compressor.	Unknown	• 15 m_N^3/h H_2 proof-of-concept unit designed and built in 2007

Oxygen production, syngas production, hydrogen production, electrical power generation	Praxair Inc., Danbury/CT, US, with partners
	Early work (ca. 1996-2001) *OTM alliance:*
	- BP p.l.c.
	- Sasol Ltd.
	- Statoil ASA
	- Foster Wheeler Ltd.
	- US DOE
	Later work on *integrated ceramic membrane system for hydrogen production*
	- US DOE
	Recent work on *oxy-fuel gasification of coal*
	- US DOE
	- NETL
		Ceramic oxygen ion-conducting membranes (*oxygen transport membranes*, OTM) for oxygen production from air (OTM oxygen), syngas generation from natural gas (OTM syngas) and oxy-fuel gasification of coal in internal gasification combined cycle (IGCC) power plants. Palladium alloy membranes for hydrogen separation (*hydrogen transport membranes*, HTM) from syngas. Multitubular reactor design.	Unknown	• Early work (1996-2001) focused on natural gas conversion to syngas
				• Later studies (2000-2008) directed to hydrogen production from natural gas
				• Recent work dedicated to oxy-fuel combustion of coal with carbon dioxide capture using OTM
				  - Stable membrane materials available
				  - O_2 flux improvements by a factor of 2 to 5 needed
				  - Pilot plant testing planned for 2009-2010

Oxygen production, electrical power generation	Air Products and Chemicals, Allentown/PA, US, with partners: - Ceramatec - Concepts NREC - Eltron Research - GE Energy - NovelEdge Technologies - PennState	Ceramic ion conducting membranes (*ion transport membranes*, ITM) for oxygen production from air, e.g., for electrical power generation in coal-based IGCC power plants. Planar membrane	2012-2015	• Project started in 1999 (11 years, 3 phases, 148 million USD) • All major phase 1 and phase 2 development objectives were met, e.g., oxygen purity > 99% for commercial-scale modules (0.5 tpd O_2), oxygen flux

	University - Siemens - SOFCo EFS (McDermott) - University of Pennsylvania - US DOE	design (wafer stack).		• higher than commercial target, successful operation of a 5 tpd O_2 prototype unit • 150 tpd O_2 pre-commercial demonstration unit currently in planning • Expansion of phase 3 planned to enable ITM Oxygen to produce large-tonnage quantities of oxygen in the FutureGen plant (see below)
Syngas production	Air Products and Chemicals, Allentown/PA, US, with partners: - Batelle (Pacific Northwest National Laboratory) - Ceramatec - Chevron-Texaco - Eltron Research Inc. - Norsk Hydro ASA - SOFCo EFS (McDermott) - PennState University - University of Alaska Fairbanks - University of Pennsylvania - US DOE	Ceramic ion conducting membranes (*ion transport membranes*, ITM) for syngas generation from natural gas (ITM Syngas). Planar design (wafer stack).	2007-2015 (as predicted in 2002)	• ITM Syngas project started in 1997 (9 years, 3 phases, 90 million USD) • High pressure membrane materials and reliable ceramic to metal seals developed • Extension needed to meet all phase 2 targets • 24000 SCFD syngas pilot-scale process development unit has demonstrated design capacity and target flux • Engineering design of 330000 SCFD syngas subscale engineering prototype initiated
Syngas production	Teikoku Oil Co. Ltd, Tokyo, Japan with partners: - Nippon Steel - NKK Steel - Japanese Ministry of Economics, Trade and Industry (METI)	Ceramic ion-conducting membrane reactor for syngas production	Unknown	Unknown
Electrical power generation	US DOE with partners (FutureGen alliance)	275 MWe coal-based IGCC power plant with CO_2 capture and storage. Plant will be configured to support R&D and	2015	The project started in 2005. The initial conceptual design was completed early in 2007, and the project is now in the design basic phase. Construction is

| | | demonstration of new technologies, including H$_2$-selective membrane reactors for pre-combustion capture of CO$_2$ and O$_2$-selective membranes (or membrane reactors) for oxy-fuel gasification. | | scheduled to start in 2009. |

2.4 Potential applications discussed in literature
(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Many applications of membrane reactors with selective membranes were proposed in the scientific literature. For a more exhaustive overview of the field the book by Sanchez Marcano and Tsotsis, 2002, a recent review by Dittmeyer and Caro, 2008, and the references therein may be consulted.

Among the proposed applications, reactors with hydrogen-selective membranes form one of the major classes. Membranes for separation of hydrogen from gas mixtures include organic polymers, solid polymer electrolytes, metals, microporous membranes, and ceramic proton conductors as well as cermets. Organic polymers are used commercially for hydrogen recovery from purge gas streams in refineries and petrochemical plants, but not in reactors because their maximum application temperature is limited to about 100°C. Solid polymer electrolytes are employed in PEMFC (polymer electrolyte membrane) and DMFC (direct methanol) fuel cells. Fuel cells, as mentioned, also belong to the class of membrane reactors and their use in electrolysis mode has been proposed, e.g., for hydrogenations, but solid electrolyte polymers like the other organic polymers suffer from limited thermal and chemical resistance which stands against a wider application in membrane reactors. Therefore, metals, microporous membranes, and the more recently developed ceramic proton conductors and cermets currently represent the most important types of membranes for hydrogen selective membrane reactors. Among these, microporous membranes, as yet, suffer from two disadvantages, i.e., only finite selectivity for hydrogen and usually poor stability in hydrothermal conditions.

Most of the proposed applications of hydrogen-selective membrane reactors concern the selective removal of hydrogen in extractor MRs. In addition, hydrogen distributor MRs with metallic membranes (mostly palladium and palladium alloys) were applied to selective hydrogenation of unsaturated hydrocarbons, e.g., acetylene, 1,3-pentadiene and cyclopentadiene and, more recently, to direct synthesis of hydrogen peroxide as well as to direct hydroxylation of aromatics with in-situ formed hydrogen peroxide (on the membrane surface in presence of gaseous oxygen). Among the hydrogen extractor MRs, dehydrogenation of alkanes, e.g., mainly cyclohexane to cyclohexene, methylcyclohexane to toluene, propane to propene, butanes to butenes, and ethylbenzene to styrene as well as dehydrogenation of alcohols was studied, i.e., 2-butanol to methyl-ethyl-ketone, isopropanol to acetone, ethanol to acetaldehyde, and methanol to methyl formate. Besides, a large number of studies were devoted to the water gas shift reaction and, by far the most, to steam reforming, mainly of methane, followed by methanol and higher hydrocarbons (LPG, gasoline and diesel components). Dry reforming of methane, i.e., converting methane

with carbon dioxide to carbon monoxide and hydrogen, was also studied in hydrogen extractor MRs.

In addition, more specialized applications involving hydrogen-selective extractor MRs have been:
- decomposition of ammonia (palladium alloy membranes)
- decomposition of hydrogen sulphide (platinum membranes)
- decomposition of hydrogen sulphide (ceramic proton-conducting solid electrolyte membranes, hydrogen removal through electrochemical pumping)
- thermal splitting of water (ceramic proton-conducting solid electrolyte membranes, hydrogen removal through electrochemical pumping)
- tritium recovery from the fusion reactor cycle (palladium alloy membranes)

Another class of membrane reactor applications relies on oxygen-selective membranes. These are mainly mixed oxygen ion and electron conducting (MIEC) ceramics and ceramic solid electrolytes. Silver also shows selective permeation of oxygen (in atomic form), but the oxygen permeance is too low for applications in membrane reactors.

As opposed to hydrogen-selective membranes, oxygen selective membranes are mainly used in distributor MRs. The most important application for MIEC membrane reactors is syngas production by partial oxidation of methane. In addition, MIEC membrane reactors are being considered for oxidative dehydrogenation of light alkanes to olefins, e.g., ethane to ethene, propane to propene, and for methane oxidative coupling to C_2-hydrocarbons.
Ceramic oxygen ion conducting solid electrolyte membranes, e.g, based on yttria- or scandia-stabilised zirconia, are normally used in solid oxide fuel cells (SOFC). The operation of SOFC systems in electrolysis mode, i.e., as an electrochemical distributor MR, was suggested for selective oxidation of hydrocarbons. Moreover, co-generation of oxygenates and electricity in SOFC systems was studied, as well as oxygen removal through electrochemical pumping in an electrochemical extractor MR for decomposition of nitrogen monoxide and sulfur dioxide as well as for thermal splitting of water.

Pervaporation membrane reactors represent another frequently studied class of extractor MRs. They have been mainly proposed for esterifications and etherifications where the produced water is removed through a hydrophilic membrane, e.g., based on polyvinylalcohol composites or microporous amorphous silica. Several industrial processes were studied, but so far no large-scale applications are reported.

Photocatalytic destruction of harmful substances combined with membrane separation is another principle; it has been proposed for water purification. Similar to an enzyme membrane reactor, such systems mostly consist of a photocatalytic reactor followed by membrane module which is connected to the reactor in a recycle configuration.

Moreover, several ideas associated with chemical conversion of carbon dioxide in membrane reactors are being pursued. These include:
- catalytic hydrogenation of carbon dioxide to methane in a hydrogen distributor MR (palladium alloy membranes)
- catalytic hydrogenation of carbon dioxide to methane and water, coupled through a palladium membrane to methane decomposition to carbon (graphite) and hydrogen
- catalytic hydrogenation of carbon monoxide to syngas, coupled through a hydrogen permeable $LaNi_5$ membrane to cyclohexane dehydrogenation

- thermal splitting of carbon dioxide with oxygen removal through electrochemical pumping in an oxygen-ion conducting solid electrolyte membrane reactor
- catalytic hydrogenation of carbon monoxide and carbon dioxide to methane with oxygen removal through electrochemical pumping in an oxygen-ion conducting solid electrolyte membrane reactor
- catalytic hydrogenation of carbon dioxide to methanol and water on Li-exchanged polyfluorinated hydrocarbon membranes which show selective permeation of methanol and water

Other proposed applications of membrane reactors include
- olefin metathesis with silicalite-1 membranes
- xylene isomerization with removal of p-xylene through MFI zeolite membranes in an extractor MR
- Fischer-Tropsch synthesis with water removal through hydrophilic zeolite or silica membranes in an extractor MR
- MTBE synthesis from tert-butanol and methanol with water removal through hydrophilic zeolite membranes in an extractor MR
- vapor phase decomposition of MTBE with methanol removal in an extractor MR

3. What are the development and application issues?

3.1 Technology development issues
(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

For different types of membrane reactors, e.g., membrane bioreactors, enzyme or chemzyme membrane reactors, pervaporation membrane reactors, and high-temperature inorganic membrane reactors, different development issues apply. The focus in Table 4 is on high-temperature membrane reactors for hydrogen production with dense metallic membranes and for syngas generation with dense mixed ion conducting ceramic membranes, as these fields currently receive the highest attention.

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Membrane materials	Highly permeable membrane materials which are stable under the conditions of the target application have to be developed.	• Should be addressed through R&D at universities and research institutes.
Membrane and module design	Commercial-scale membranes and membrane modules must be designed to achieve high permeation fluxes, i.e., the mass transfer resistance in the support and in the channels for distributing the flow must be minimized. Heat transfer and pressure drop also have to be considered. The design must be cost-effective, i.e., support and technologies used for membrane formation	• Should be addressed through R&D. • Membrane producers and research institutes or universities should work together on these issues. • Modelling of the relevant phenomena is

Challenge	Description	How and by whom should the challenge be addressed?
	must be affordable.	essential.
Membrane quality	Defect-free coating of porous substrates with thin ceramic or metallic films, or fabrication of thin free-standing membrane foils for stacked designs must be achieved on commercial scale.	• Should be addressed through R&D, mainly by membrane producers. • Improved methods for manufacturing are required.
Membrane degradation under process conditions	Degradation of the performance due to poisoning of the membrane surface by contaminants and to solid-state reactions (or diffusion) between the support and the membrane layer must be kept within acceptable limits. Membranes must not develop defects or deteriorate otherwise when applied to process conditions.	• Should be addressed through collaborative R&D and demonstration projects involving universities, research institutes and membrane producers.
Sealing	Reliable seals for connecting inorganic membranes to modules and module housings must be developed which can withstand high temperature as well as the process atmosphere, and which allow joining of different materials, e.g., ceramics to metals.	• Should be addressed by membrane producers and end users through collaborative R&D.
Membrane lifetime	Long membrane life must be demonstrated for key applications to build up confidence in the new technology. For catalytic membranes, strategies for regeneration and, eventually, recycling are needed.	• Should be adressed by collaborative projects on key applications involving membrane producers, technology providers and end users.
Membrane reactor design and scale-up	MR performance depends on the kinetics of reactions and transport processes at various levels. MRs, like other reactors, should be designed based on such knowledge. Scale-up must be demonstrated to build up confidence in the new technology.	• Should be addressed by research institutes, universities and companies when developing new applications. • Modelling combined with experimental data from various scales is essential.

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Membrane availability	Commercial-scale facilities for cost-efficient production of inorganic membranes must be established in order to enable the supply of large membrane areas required for industrial-scale plants. Significant investment will be needed.	• Membrane producers, catalyst suppliers or technology developers are expected to undertake these investments.
Membrane (module) cost	Cost-effective membrane materials, membrane supports and fabrication methods are required	• Should be addressed through R&D by

	to limit the investment costs for large-scale applications. Reactor design and sealing concepts also have to consider the cost issue.	Universities, research institutes, technology developers and membrane producers.
Robustness	Membrane modules must not be fragile as they have to withstand severe conditions in any realistic process environment (high temperature, thermal and mechanical stresses, flow-induced, vibration, etc.).	• Should be addressed through collabroative R&D projects.
Acceptance	Membrane reactors represent a revolutionary technology. Confidence must be built up by demonstration projects and successful applications in smaller scale.	• Should be addressed by demonstration projects.
Plant size	Large-scale applications, e.g., in IGCC power plants or the synthesis of bulk chemicals are extremely challenging as they call for very high investment and do not tolerate downtime.	• Scale-up strategy must take care of controlling the risk of the first full-scale installation.

4. Where can information be found?

4.1 Key publications
(Provide the list of key publications in Table 6)

There are numerous publications and reviews on selective membrane reactors available in the scientific literature.

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
M.C. Porter (Ed.), *Handbook of Industrial Membrane Technology*, Noyes Publications, Park Ridge, 1990, pp. 604.	Book	Overview of the use of polymeric membranes for separations.
Simon Judd (Ed.), *The MBR Book. Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment*, Elsevier Science, Amsterdam, 2006, pp. 344.	Book	Exhaustive treatment of membrane bioreactors.
J. Wöltinger, K.-H. Drauz, A.S. Bommarius, *The membrane reactor in the fine chemicals industry*, Appl. Catal. A: Gen. **221** (2001) 171-185. J. Wöltinger, A. Karau, W. Leuchtenberger, K. Drauz, *Membrane Reactors at Degussa*, Advances in Biochemical Engineering and Biotechnology **92** (2005) 289-316.	Review	Enzyme/chemzyme membrane reactors from an industrial perspective.
Y. Zhu, R.G. Minet, T.T. Tsotsis, *A continuous pervaporation membrane reactor for the study of esterification reactions using a composite polymeric/ceramic membrane*, Chem. Eng. Sci. **51** (1996) 4103-4113.	Paper	Comprehensive discussion of pervaporation membrane reactors for esterifications.
F. Lipnizki, S. Hausmanns, G. Laufenberg, R. Field, B. Kunz, *Use of pervaporation/bioreactor hybrid processes in biotechnology*, Chem. Eng. Technol. **70** (1998) 1587-1595.	Review	Pervaporation membrane reactors for biotechnological applications.

F. Lipnizki, R.W. Field, P.K. Ten, *Pervaporation-based hybrid processes: A review of process design applications and economics*, J. Membr. Sci. **153** (1999) 183-210.	Review	Industrial applications of pervaporation processes combined with distillation or chemical reaction.
S.Y. Lim, B. Park, F. Hung, M. Sahimi, T.T. Tsotsis, *Design issues of pervaporation membrane reactors for esterification*, Chem. Eng. Sci. **57** (2002) 4933-4946.	Paper	Instructive model-based analysis of different configurations of pervaporation membrane reactors.
H.E.A. Brüschke, *State-of-the-Art of Pervaporation Processes in the Chemical Industry* in: S. Pereira Nunes, K.-V. Peinemann (eds.), *Membrane Technology in the Chemical Industry*, Wiley-VCH, Weinheim, 2006, pp. 151-202.	Review / Book Chapter	Pervporation membrane reactors from an industrial perspective.
V. M. Gryaznov, *Hydrogen Permeable Palladium Membrane Catalysts*, Plat. Met. Rev. **30** (1986) 68-72.	Review	Collection of work on Pd alloy membranes mainly for selective hydrogenation.
V. M. Gryaznov, *Platinum Metals as Components of Catalyst-Membrane Systems*, Plat. Met. Rev. **36** (1992) 70-79.	Review	Assessment of different membrane reactors types for improving catalytic reactions involving hydrogen.
E. Kikuchi, *Hydrogen permselective membrane reactors*, CATTECH **1** (1997) 67-74.	Review	Information on the Pd alloy membrane reformer developed by Mitsubishi Heavy Industries and Tokyo Gas (early phase).
V.M. Gryaznov, N.V. Orekhova, *Reactors with Metal and Metal-Containing Membranes* in: A. Czybulski, J. Moulijn (eds.), *Structured Catalysts and Reactors*, Marcel Dekker, New York, 1998, Chapter 16, pp. 435-461.	Review	Overview of membrane reactors with Pd alloy membranes for hydrogenation and dehydrogenation.
R. Dittmeyer, V. Höllein, K. Daub, *Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium*, J. Mol. Catal. A: Chem. **173** (2001) 135-184.	Review	Evaluation of the published experimental work on dehydrogenation and hydrogenation membrane reactors with Pd-alloy membranes.
S.N. Paglieri, J.D. Way, *Innovations in Palladium Membrane Research*, Sep. Purif. Methods **31** (2002) 1-169	Review	Extensive review on all aspects of Pd-based membranes with more than 1400 references.
S. Uemiya, *State-of-the-art of supported metal membranes for gas separation*, Sep. Purif. Methods **28** (1999) 51-85.	Review	Reviews mainly focused on steam steam reforming of

S. Uemiya, *Brief review of steam reforming using a metal membrane reactor*, Topics Catal. **29** (2004) 79-84.		hydrocarbons in metal MRs.
Y. Teraoka, H.-M. Zhang, S. Furukawa, N. Yamazoe, *Oxygen permeation through perovskite-type oxides*, Chem. Lett. 1985, 1743-1746. Y. Teraoka, T. Nobunaga, N. Yamazoe, *Effect of Cation substitution on the oxygen semipermeability of perovskite-type oxides*, Chem. Lett. 1988, 503-506.	Papers	Pioneering studies on mixed oxygen ion and electron conduction in complex ceramic oxides.
H.J.M. Bouwmeester, A.J. Burggraaf, *Dense Ceramic Membranes for Oxygen Separation*, in: A.J. Burggraaf, L. Cot (Eds.), *Fundamentals of Inorganic Membrane Science and Technology*, Membrane Science and Technology Series Vol. 4, Elsevier, Amsterdam, 1996, 435-528.	Book Chapter / Review	Instructive description of the theory and good analysis of the developments up to 1995.
P.N. Dyer, R.E. Richards, S.L. Russek, D.M. Taylor, *Ion transport membrane technology for oxygen separation and syngas production*, Solid State Ionics **134** (2000) 21-33.	Review	Information on the ion transport membrane developments pursued by Air Products.
J.H. Tong, W.S. Yang, R. Cai, B.C. Zhu, W. Lin, *Novel and Ideal Zirconium-Based Dense Membrane Reactors for Partial Oxidation of Methane to Syngas*, Catal. Lett. **78** (2002) 129-137.	Paper	First mention of BCFZ as a promising new perovskite material for syngas production.
H.J.M. Bouwmeester, *Dense Ceramic Membranes for Methane Conversion*, Catal. Today 82 (2003) 141-150.	Review	Review on ion conducting membrane reactors for syngas generation and other methane conversion reactions.
J. Caro, H. Wang, C. Tablet, A. Kleinert, A. Feldhoff, T. Schiestel, M. Kilgus, P. Kölsch, S. Werth, *Evaluation of perovskites in hollow-fibre and disk geometry in catalytic membrane reactors and in oxygen separators*, Catal. Today **118** (2006) 128-135.	Paper	BCFZ perovskite hollow-fibres made by phase inversion spinning reached very high, stable O_2 fluxes in a syngas environment.
J. Sanchez Marcano, T.T. Tsotsis, *Catalytic Membranes and Membrane Reactors*, Viley-VCH, Weinheim, 2002, pp. 251.	Book	Exhaustive analysis of the whole field of catalytic membrane reactors including modelling and economic and technical feasibility issues.
A.G. Dixon, *Recent Research in Catalytic Inorganic Membrane Reactors*, International Journal of Chemical Reactor Engineering, Vol. 1, 2003, R6.	Review	Good review on inorganic membrane reactors covering the period 1998-2003.

R. Dittmeyer, K. Svajda, M. Reif, *A review of catalytic membrane layers for gas/liquid reactions*, Top. Catal. **29** (2004) 3-27.	Review	Assessment of reactor concepts for solid-catalyzed gas/liquid reactions based on catalytic membranes.
A. F. Sammells, M. V. Mundschau, *Nonporous Inorganic Membranes for Chemicals Processing*, Wiley-VCH, Weinheim, 2006, pp. 277.	Book	Overview of recent developments in dense inorganic membranes for hydrogen and oxygen transport, respectively, i.e., ceramic proton conductors, Pd-based and group Vb metallic membranes, oxygen ion- and mixed conducting ceramics. Engineering and economic considerations are included.
R. Dittmeyer, J. Caro, *Catalytic Membrane Reactors* in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (eds.), Handbook of Heterogeneous Catalysis, 2nd ed., Wiley-VCH, Weinheim, 2008, Chapter 10.7., pp. 50.	Review	MR concepts and present status of the most important applications.

4.2 Relevant patents and patent holders
(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Numerous patents and patent applications exist describing the use of selective membrane reactors for a multitude of applications. An area that has seen intensive patenting over the last years are membrane bioreactors. For example, a search with "Membrane Bioreactor" in the title yields 205 patents and patent applications since 1983, most of which have been filed later than the year 2000. Asia ranges on the first place (CN: 37, KR: 25, JP: 15) followed by America (US: 44, CA: 14) and the European Union (EP: 25). Water and wastewater treatment is the dominating application. More recent patents focus on improved fouling control and reduced energy consumption.

Ceramic ion transport membranes, mainly for oxygen permeation, but more recently also for hydrogen transport, represent another field with particularly high patenting activity over the last decade. For example, Air Products and Chemicals, one of the key developers of oxygen ion transport membranes for IGCC power plants and syngas production alone has been granted more than 47 U.S. patents in the field of ion transport membranes together with their equivalent patents in many other countries (Dyer et al., 2000).

Table 7 gives some examples for relevant patents for the different types of membrane reactors, i.e., membrane bioreactors, enzyme membrane reactors, pervaporation membrane reactors, hydrogen transport membrane reactors (mainly dehydrogenation), oxygen transport membrane reactors, and extractor-type porous membrane reactors for selected applications.

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
US 3 186 917 (filed: 18.04.1962) *Process and Apparatus for Dialysis Fermentation*	Biochemical Processes, Inc., New York/NY, US.	Early patent disclosing a membrane bioreactor for continuous fermentation.
US 3 915 802 (filed: 19.08.1974) *Dialysis Process and Apparatus*	The Upjohn Company, Kalamazoo/MI, US.	Membrane bioreactor for production of the antibiotic cycloheximide.
US 4 636 473 (filed: 06.10.1983) *Membrane and Static Mixer-Moderated Bioreactor with Antifouling Device*	Rensselaer Polytechnic Institute, Troy/NY, US.	Membrane bioreactor with flow reversal to prevent fouling.
US 4 910 139 (filed: 01.08.1988) *Method for Continuously Producing Citric Acid by Dual Hollow Fiber Membrane Bioreactor*	Korea Advanced Institute of Science and Technology, Seoul, KR.	Membrane bioreactor with two membranes for optimization of the cell growth, i.e., one for withdrawing the product and one for supplying oxygen.
US 5 204 001 (filed: 09.10.1991) *Membrane Bioreactor System for Treating Synthetic Metal-Working Fluids and oil-Based Products*	Zenon Environmental Inc., Burlington, CA.	Membrane bioreactor system for treatment of wastewaters containing a mixture of easily biodegradable fats and oils, much less easily biodegradable synthetic fluids, oils and greases and non-biodegradable solids.
US 5 254 253 (filed: 21.08.1992) *Modular Shipboard Membrane Bioreactor System for Combined Wastewater Streams*	Zenon Environmental Inc., Burlington, CA.	Membrane bioreactor system for treatment of mixed wastewater on ships (toilet, shower, bilge water).
EP 0 510 328 B1 (filed: 26.02.1992) *Apparatus for Treating Activated Sludge*	Kubota Corp., Osaka, JP.	Airlift membrane bioreactor.
US 6 767 455 B2 (filed: 30.09.2002) *Airlift Membrane Device and Membrane Bioreactor and Bioreactor Process Containing Same*	CeraMem Corp., Waltham/MA, US.	Airlift membrane bioreactor based on ceramic filters.
US 6 863 817 B2 (filed: 05.12.2002) *Membrane Bioreactor, Process and Aerator*	Zenon Environmental Inc., Oakville, CA.	Improved aerated membrane bioreactor system.
WO 96/11256 (filed: 11.10.1994) *Process for the continuous enzymatic extraction of hydrophobic products and device suitable therefore*	Forschungszentrum Jülich GmbH, Jülich, DE	Extractor-type enzyme MR process based on a hydrophobic membrane contactor. An organic product is continuously withdrawn from the homogeneous aqueous enzyme-containing reaction mixture.

US 2 956 070 (filed: 29.04.1958) *Organic chemical reactions involving liberation of water*	The American Oil Company, Texas City/TX, US.	Early patent on pervaporation membrane reactors.
EP 0 210 055 A1 (filed: 17.07.1985) *Esterification Process*	BP Chemicals Ltd., London, GB.	Pervaporation membrane reactors for production of liquid esters.
US 4 774 365 (filed: 25.11.1987) *Pervaporation Process for Separating Alcohols from Ethers*	Air Products and Chemicals, Inc., Allentown/PA, US.	Pervaporation membrane reactor process for etherification reactions.
WO 03/013685 (filed: 06.08.2001) *Removal and Recovery of Solutes Present in Ionic Liquids by Pervaporation*	Instituto de Biologia Experimental e Técnologia (IBET), Oeiras, PT.	Method for preparation and purification of ionic liquids by pervaporation as well as reactive applications of them.
US 6 639 108 B2 (filed: 03.09.2002) *Ammoximation of Ketones and Work-up by Pervaporation/Vapor Permeation*	Degussa AG, Düsseldorf, DE.	Pervaporation membrane reactor process for ammoximation of ketones using a homogeneous catalyst.
US 3 290 406 (filed: 02.06.1965) Process for Dehydrogenation	Engelhard Industries, Inc., Newark/NJ, US.	Early US patent on hydrocarbon dehydrogenation in palladium membrane reactors (including oxidation of the permeated hydrogen at the membrane surface).
GB 1 199 683 (filed: 08.03.1968) *A process for Dehydrogenation, Dehydrocyclization or Hydrodealkylation of Hydrocarbons* US 3 562 346 (filed: 08.03.1968) *Process for Dehydrogenation, Dehydrocyclization and Hydrodealkylation of Hydrocarbons* GB 1 299 540 (filed: 01.04.1970) *Dehydrogenation, Dehydrocyclization and Hydrodealkylation Catalysts*	A.V. Topchiev Institute of Petrochemical Synthesis, Moscow, RU.	Early patents on hydrocarbon dehydrogenation in palladium membrane reactors.
US 4 791 079 (filed: 09.06.1986) *Ceramic Membrane for Hydrocarbon Conversion*	Arco Chemical Co., Newtown Square/PA, US.	Early patent disclosing the use of a mixed oxygen ion and electron conducting ceramic membrane (Ti-doped Y-stabilized ZrO_2 membrane on Mg-stabilized ZrO_2 support; coating was done by electrochemical vapor deposition) for hydrocarbon oxidation and dehydrogenation.
US 6 200 541 B1 (filed: 07.05.1999) *Composite Materials for Membrane Reactors*	BP Amoco Corp., Chicago/IL, US.	Highly oxygen permeable membrane based on $SrCoFe_{0.5}O_x$

		on mechanically robust sinter metal support (316L, Incoloy 800HT or Haynes 230 nickel superalloy). Membrane coating was done by thermal spraying.
US 6 565 632 B1 (filed: 17.12.2001) *Ion-Transport Membrane Assembly Incorporating Internal Support*	Praxair Inc., Danbury/CT, US.	Internally supported tubular membrane to prevent damage of the tube by creep buckling under external pressure.
WO 03/033985 A1 (filed: 25.09.2002) *Method and Equipment for Feeding two Gases into and out of a Multichannel Monolithic Structure* EP 1 444 475 B1 (filed: 25.09.2002) *Monolithic System, Method for Mass and/or Heat Transfer and Plant Therefore*	Norsk Hydro ASA, Oslo, N	Monolithic membrane design developed by Norsk Hydro.
DE 100 56 787 A1 (filed: 16.11.2000) *Reaktor* DE 101 14 173 A1 (filed: 23.03.2001) *Reaktor*	Linde AG, Wiesbaden, DE	Tubular membrane reactor design for syngas production developed by Linde.
US 2003/0039601 A1 (filed: 10.08.2001) *Oxygen Ion Transport Membrane Apparatus and Process for Use in Syngas Production*	Praxair Inc., Danbury/CT, US.	Alternative tubular membrane reactor design published by Praxair.
US 2005/0031531 A1 (filed: 06.08.2003) *Ion Transport Membrane Module and Vessel System*	Air Products and Chemicals, Inc., Allentown/PA, US.	Planar membrane reactor design developed by Air Products.
JP 299545/85 (filed: 28.12.85) EP 0 228 885 B1 (filed: 22.12.86) *Use of Porous Membrane in Reaction Progress*	NGK Insulators, Ltd., Aichi, JP	Early patent on a selective (Knudsen diffusion) extractor-type membrane reactor.
JP 2001009265 A (filed: 28.06.1999) *Catalytic Device for Methanol Synthesis and Method for Synthesizing Methanol*	Mitsubishi Heavy Industries Ltd., Tokyo, JP.	Extractor-type selective porous catalytic membrane reactor for methanol synthesis.
WO 02/102710 A1 (filed: 15.06.2001) *Catalytic Membrane Reactor that is used for the Decomposition of Hydrogen Sulphide into Hydrogen and Sulphur and the Separation of the Products of said Decomposition*	David Systems & Technology S.L., Madrid, ES.	Catalytic and permselective extractor-type membrane reactor for H_2S decomposition.
US 6 403 660 B1 (filed: 05.12.2000) *Production of hydrocarbons*	Sasol Technology Ltd., Johannesburg/ZA.	Extractor-type membrane reactor for Fischer-Tropsch-Synthesis.

4.3 Institutes/companies working on the technology
(Provide the list of most important research centers and companies in Table 8)

Many institutes and companies worldwide work on the different types of selective membrane reactors discussed in this report. It is impossible here to list all relevant institutions. Instead, Table 8 focuses mainly on academic groups (universities and research institutes) active in the development of hydrogen or oxygen transport membrane reactors. Industrial companies developing the technology and such who might potentially use it in the future are listed in Table 9. Institutions from Europe and from the United States dominate to a certain extent, mainly due to a lack of insight in the situation in Asia and other parts of the world. Moreover, the list is certainly incomplete concerning the activities undertaken by industry, as these are less well documented in the accessible scientific literature. The list is based at least partly on the number of publications in the field issued, i.e., since the year 2000. However, some of the groups may have stopped or redirected their activities in the meantime.

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Instituto de Investigaciones en Catálisis y Petroquimica, Santiago del Estero (J. Munera, L.M. Cornaglia, E.A. Lombardo)	Argentina	• Pd based hydrogen selective membranes for steam reforming
The University of Queensland, Centre for Functional Nanomaterials, Brisbane (J.C.D. da Costa)	Australia	• Hydrogen selective membranes for water gas shift membrane reactors
CANMET Energy Technology Centre-Ottawa, Ottawa (J. Galuszka)	Canada	• Hydrogen selective membrane reactor (molecular sieve silica membranes) for catalytic partial oxidation or dry reforming of natural gas to syngas
Laval University, Department of Chemical Engineering, Québec (S. Kaliaguine)	Canada	• Permselective membrane reactors (Pd-alloy membranes, ceramic oxygen ion conducting membranes, polymeric membranes)
University of British Columbia, Department of Chemical and Biochemical Engineering, Vancouver (J.R. Grace)	Canada	• Hydrogen selective membranes for steam reforming (research partner of MRT, see Table 9)
University of Western Ontario, Chemical Reactor Engineering Centre, London/Ontario (H. de Lasa)	Canada	• Pd-alloy based hydrogen selective membranes for steam reforming of methane
Dalian Institute of Chemical Physics, Chinese Academy of Sciences (W. Yang, G. Xiong)	P.R. China	• Hydrogen and oxygen selective membranes, i.e., for extractor and distributor MRs (partial oxidation, steam and carbon dioxide reforming, oxidative

		dehydrogenation of hydrocarbons)
University of Science and Technology of China, Department of Materials Science and Engineering, Hefei (C.S. Chen, Q. Wei)	P.R. China	• Pd alloy based hydrogen selective membranes for methane steam reforming • Dense perovskite oxygen selective membranes for partial oxidation of methane and oxidative dehydrogenation of paraffins
Nanjing University of Technology, Membrane Science and Technology Research Center, Nanjing (N. Xu), College of Materials Science and Engineering, Nanjing (N. Yang)	P.R. China	• Dense perovskite oxygen selective membranes for partial oxidation of methane and oxidative dehydrogenation of paraffins
Tsinghua University, Department of Materials Science, Beijing (X.Q. Tong)	P.R. China	• Pd-alloy based hydrogen selective membranes
The Hong Kong University of Science and Technology, Department of Chemical Engineering (K. L. Yeung)	P.R. China	• Microfabricated membranes (zeolites, etc.) • Microstuctured membrane reactors
Institut Européen des Membranes, Montpellier (J. Sanchez, A. Julbe)	France	• Porous and dense ceramic and hybrid membranes for separation of gases and vapours • Enzymatic membrane reactors • Bioinspired membranes and interfaces • Catalytic membrane reactors • Modelling of membrane processes
Institut de Recherches sur la Catalyse et l'Environnement (IRCE), Villeurbanne (J.-A. Dalmon, S. Miachon)	France	• Porous membranes for gas separation • Pd-alloy based composite membranes for hydrogen separation • Dense membranes for oxidations at short contact time
Université des Sciences et Technologies de Lille, Villeneuve d'Ascq (É. Bordes-Richard)	France	• Dense catalytic membranes for selective oxidation of alkanes
RWTH Aachen, Institute of Process Engineering (Th. Melin)	Germany	• Membrane processes (including modelling of membrane mass transport) • Membrane bioreactors • Permselective membrane reactors
Forschungszentrum Jülich, Institut für Biotechnologie 2, Jülich (Ch. Wandrey)	Germany	• Enzyme and chemzyme membrane reactors
Universität Rostock, Institut für Chemie, Technische Chemie, Rostock (U. Kragl)	Germany	• Enzyme membrane reactors

Max-Planck-Institut für Dynamik komplexer technischer Systeme, Magdeburg (K. Sundmacher)	Germany	• Electrocatalytic membrane reactors • Modelling and systems analysis of membrane reactors
Forschungszentrum Jülich, Institut für Werkstoffe und Verfahren der Energietechnik, Jülich (W. Meulenberg)	Germany	• Inorganic membranes for gas separation (microporous membranes, mixed ion and electron conducting ceramics)
DECHEMA e.V., Karl-Winnacker-Institut, Technical Chemistry, Frankfurt am Main (R. Dittmeyer)	Germany	• Hydrogen permeable membranes (Pd-alloy based composite membranes) for extractor membrane reactors
Fraunhofer Institut für Grenzflächen- und Bioverfahrenstechnik IGB, Stuttgart (Th. Schiestel)	Germany	• Supported Pd-alloy membranes • Mixed oxygen ion and electron conducting ceramic hollow-fiber membranes
University of Hannover, Institut für Physikalische Chemie und Elektrochemie, Hannover (J. Caro)	Germany	• Mixed oxygen ion and electron conducting membrane reactors
Hermsdorfer Institut für Technische Keramik e.V., Hermsdorf (I. Voigt)	Germany	• Mixed oxygen ion and electron conducting membranes
Aristotle University of Athens, Dhemical Engineering Department, Athens (M. Stoukides)	Greece	• Electrocatalytic membrane reactors
ENEA, Centro Ricerche di Frascati, Rome (V. Violante, S. Tosti)	Italy	• Pd based hydrogen selective membranes and their use in water gas shift membrane reactors
Università di Genova, Laboratorio di Scienze e Tecnologie Chimiche e dei Materiali "SCITECHMA" (G. Capannelli, A. Comite)	Italy	• Membrane preparation • Catalytic membrane reactors (extractors, distributors) • Modelling of membrane reactors
Institute on Membrane Technology, Arcavacata di Rende (E. Drioli, A. Basile, G. Barbieri)	Italy	• Preparation and transport phenomena in inorganic, polymeric and biological membranes • Molecular membrane operations and integrated processes for chemicals production and biomedical applications • Catalytic membranes and membrane reactors (reforming, water gas shift reaction, etc.)
Utsunomiya University, Department of Applied Chemistry (N. Itoh)	Japan	• Pd-alloy based membrane reactors for dehydrogenation, reforming, and other reactions

National Institute of Advanced Industrial Science and Technology (AIST), Sendai (F. Mizukami)	Japan	• Pd-alloy based membrane reactors for direct hydroxylation of aromatics and other reactions
National Institute for Materials Science, Tskukuba (C. Nishimura)	Japan	• Pd based hydrogen selective membranes
Chiba Institute of Technology, Narashino (S. Yamaguchi)	Japan	• Pd based hydrogen selective membranes
Hiroshima University, Department of Chemical Engineering, Hiroshima (T. Tsuru)	Japan	• Porous inorganic hydrogen selective membranes for steam reforming
The University of Tokyo, Department of Chemical System Engineering, Tokyo (T. Yamaguchi)	Japan	• Hydrogen selective membranes for steam reforming
Research Institute of Innovative Technology for the Earth, Kyoto (Y. Matsumuura)	Japan	• Hydrogen selective membranes for steam reforming
Kyushu University, Department of Applied Chemistry, Fukuoka (K. Kusakabe)	Japan	• Porous inorganic hydrogen selective membranes
Japan Atomic Energy Research Institute, Department of Advanced Nuclear Heat Technology, Ibaraki (M. Nomura)	Japan	• Porous inorganic hydrogen selective membranes
Tohoku University, Institute for Materials Research, Katahira (S. Yamaura)	Japan	• Porous inorganic hydrogen selective membranes
Energy Research Centre of the Netherlands ECN, Petten (A. de Groot)	The Netherlands	• Composite Pd-alloy membranes and membrane reactors for hydrogen extraction from steam reforming, dehydrogenation and other reactions • Microporous membranes for hydrogen separation and water gas shift membrane reactors
Twente University, Membrane Technology Group, Enschede (Matthias Wessling, Henny Bouwmeester) MESA Research Institute, Enschede (H.D. Tong, N.E. Benes)	The Netherlands	• Porous and dense inorganic membranes for gas separation • Membrane microreactors • Biomedical membrane applications • Microstructured Pd-alloy membranes
Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Eindhoven (J. Keurentjies, F.C. Gielens)	The Netherlands	• Pervaporation membrane reactors • Microstructured Pd based membranes
Delft University of Technology, DelftChemTech, Reactor & Catalysis Engineering, Delft (F. Kapteijn)	The Netherlands	• Zeolite membrane reactors
TNO Institute of Environmental Science, Apeldoorn	The Netherlands	• Membrane bioreactors

SINTEF Materials and Chemistry, Oslo, (R. Bredesen)	Norway	• Porous and dense membranes for gas separation • Catalytic membrane reactors for methane reforming
University of Oslo, Center for Materials Science and Nanotechnology, Oslo (T. Norby)	Norway	• Proton conducting ceramic membranes and membrane reactors
Universidade Nova de Lisboa, Departamento de Química, REQUIMTE/CQFB, Caparica (J. G. Crespo, J. Vital)	Portugal	• Membrane bioreactors • Polymeric catalytic membranes for fine chemistry applications • Pervaporation membrane reactors
University of Aveiro, Department of Ceramics and Glass Engineering, Aveiro (V.V. Kharton, A.A. Yaremchenko, J.R. Frade)	Portugal	• Dense perovskite oxygen selective membranes for partial oxidation of methane and oxidative dehydrogenation of paraffins
A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow (V. Volkov , V. Teplyakov)	Russia	• Catalytic membranes and catalytic membrane reactors
King Saud University, Department of Chemical Engineering, Riyahd (M.E.E. Abashar)	Saudi Arabia	• Hydrogen selective membranes for steam reforming
Korean Research Institute of Chemical Technology, Membrane and Separation Research Center, Daejeon (K.H. Lee)	South Korea	• Pd based hydrogen selective membranes • Porous inorganic hydrogen selective membranes • Membrane reformer for methanol
Korea Institute of Energy Research, Hydrogen Energy Research Center, Daejeon (G.J. Hwang) Energy Materials Research Team, Daejeon (K.S. Lee)	South Korea	• Porous inorganic hydrogen selective membranes • Dense perovskite oxygen selective membranes for partial oxidation of methane and oxidative dehydrogenation of paraffins
University of Zaragoza, Department of Chemical and Environmental Engineering (J. Santamaria, M. Menendez)	Spain	• Inorganic membranes (zeolites and other) for pervaporation and separation of gases and vapours • Catalytic membrane reactors (distributors, extractors)
Laboratoire d'Energetique Industrielle, Lausanne (S. Diethelm)	Switzerland	• Dense perovskite oxygen permeable membranes for partial oxidation of methane and oxidative dehydrogenation of paraffins

National Cheng Kung University, Department of Chemical Engineering, Tainan (H.I. Chen, T.C. Huang)	Taiwan	• Pd based hydrogen selective membranes
Industrial Technology Research Institute, Center for Environmental, Safety and Health Technology Development, Chutung (Y.M. Lin)	Taiwan	• Hydrogen selective membranes for steam reforming
Cranfield University, School of Applied Sciences, Centre for Water Science	United Kingdom	• Membrane bioreactors
University of Bath, Department of Chemical Engineering, Bath (J.A. Howell)	United Kingdom	• Membrane bioreactors
Robert Gordon University, Centre for Process Integration and Membrane Technology, Aberdeen (E. Gobina)	United Kingdom	• Membrane reactor catalysis
Auburn University, Department of Chemical Engineering, Auburn/AL (Z.X. Chen, S.S.E.H. Elnashaie, P. Prasad)	United States	• Hydrogen selective membranes for steam reforming
Center for Inorganic Membrane Studies (CIMS), Department of Chemical Engineering, Worcester Polytechnique Institute, Worcester/MA, (Y.H. Ma)	United States	• Dense and microporous inorganic membranes • Palladium alloy composite membranes for hydrogen separation • Membrane reactors
Arizona State University, Department of Chemical Engineering, Materials for Separation Laboratory, Tempe/AR (Y.S. Lin, before: University of Cincinnati, Department of Chemical Engineering)	United States	• Dense perovskite oxygen selective membranes for partial oxidation of methane and oxidative dehydrogenation • Pd based hydrogen selective membranes • Ceramic proton conducting hydrogen selective membranes
Colorado School of Mines, Department of Chemical Engineering, Golden/CO (D. Way)	United States	• Pd based hydrogen selective membranes • Hydrogen selective membranes for water gas shift membrane reactors
National Energy Technology Laboratory (NETL), US Department of Energy, Pittsburgh/PA (K.S. Rothenberger)	United States	• Pd based hydrogen selective membranes
Oak Ridge National Laboratory, Oak Ridge/TN, Fuel cells and functional materials (T.R. Armstrong)	United States	• Ceramic proton conducting membranes for hydrogen separation • Low-cost fabrication methods for gas separation membranes and catalytic membranes
Los Alamos National Laboratory, Los Alamos/NM (S.A. Birdsell, S. Paglieri)	United States	• Pd-alloy based hydrogen permeable membranes

Argonne National Laboratory, Argonne/IL, Energy Systems (U. Balachandran)	United States	• Ceramic mixed ion and electron conducting oxygen selective or hydrogen selective membranes
Virginia Tech, Department of Chemical Engineering, Blacksburg (S.T. Oyama)	United States	• Porous inorganic hydrogen selective membranes • Hydrogen selective membranes for steam reforming
University of Southern California, Department of Chemical Engineering, Los Angeles (T.T. Tsotsis)	United States	• Porous inorganic hydrogen selective membranes for steam reforming
Gas Technology Institute, Chicago/IL (S.J. Doong, F. Lau, E. Ong)	United States	• Ceramic proton conducting membrane reactor for hydrogen production from coal
University of Florida, Department of Materials Science & Engineering, Gainesville (E.D. Wachsman)	United States	• Ceramic proton conducting membrane reactor for hydrogen production from coal
Southwest Research Institute, San Antonio/TX (K. Coulter)	United States	• Self supporting Pd-alloy membranes for efficient production of coal derived hydrogen
The Pennsylvania State University, Materials Research Institute, University Park/PA (R.E. Tressler)	United States	• Mixed ion and oxygen conducting ceramic membranes for oxygen transport
University of Pennsylvania, Materials Research and Engineering Center, Philadelphia/PA	United States	• Mixed ion and oxygen conducting ceramic membranes for oxygen transport
University of Alaska Fairbanks, Department of Mechanical Engineering, Fairbanks/AK (D. Das)	United States	• Mixed ion and oxygen conducting ceramic membranes for oxygen transport

5. Stakeholders

Dense and porous polymeric membranes and conventional porous ceramic membranes for membrane bioreactors and enzyme or chemzyme membrane reactors are available today from different suppliers (see, for example, Porter, 1990, Pereira-Nunes and Peinemann, 2006). In contrast, thin-film metal composite membranes (Pd alloys) for hydrogen separation cannot be obtained in large quantities on a regular commercial basis, and microporous or dense mixed proton and electron conducting ceramic membranes for hydrogen separation as well as dense mixed oxygen and electron conducting membranes for oxygen separation have not yet reached commercial status. These materials are currently beeing developed in industry-led R&D consortia involving membrane manufacturers, academic research institutes, engineering companies and end users. Table 9 provides a list of companies known to be active in these fields. For membrane bioreactors applied to water and wastewater treatment, which have already reached some commercial success, the major vendors were given already in Table 2.

5.1 Suppliers and developers
(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	Country	Remarks
Membrane Reactor Technology Ltd., Vancouver	Canada	Research-oriented small company developing a fluidized bed membrane reactor (foils and supported thin-film membranes based on Pd-alloys) for hydrogen production from methane (demonstration unit with 15 m_N^3/h H_2 reported, see Table 3)
W.C. Hereaus GmbH, Engineered Materials Division, Hanau	Germany	Noble metal and catalyst producer offering a metal-supported Pd-alloy membrane for application in the generation of hydrogen for fuel cells
Evonik Degussa GmbH, Hanau	Germany	Producer of fine chemicals developing processes based on enzyme/chemzyme membrane reactors for commercial use
Uhde GmbH, Dortmund	Germany	Engineering company active in the development of mixed oxygen ion and electron conducting membrane reactors for oxygen enrichment and syngas generation (perovskite hollow fiber membranes)
Linde Group, Engineering Division, Pullach	Germany	Engineering company active in the development of mixed oxygen ion and electron conducting membrane reactors for syngas generation and of metal-supported Pd-alloy membrane reactors for hydrogen production
Tokyo Gas Co. Ltd., Tokyo	Japan	Gas supplier developing a packed-bed membrane reformer for local hydrogen production from city gas (see Table 3)
Mitsubishi Heavy Industries Ltd., Tokyo	Japan	Engineering company developing a packed-bed membrane reformer for local hydrogen production from city gas (see Table 3)
Norsk Hydro ASA, Oslo	Norway	Engineering company active in the development of oxygen transport membrane reactors for syngas generation from natural gas

Sulzer Chemtech, Winterthur	Switzerland	Engineering company developing pervaporation and vapor permeation processes for separation and combined reaction/separation
Wellman CJB, Portsmouth	United Kingdom	Company developing hydrogen generators based on Pd-alloy membranes
Membrane Technology and Research Inc., Menlo Park/CA	United States	Company developing polymeric membrane separation technologies
Media and Process Technology, Pittsburgh/PA	United States	Company developing porous silicon carbide and carbon hydrogen selective membranes
Air Products and Chemicals, Inc., Allentown/PA	United States	Global gas and chemicals producer developing ceramic mixed oxygen ion and electron conducting membranes for oxygen production and syngas generation in membrane reactors (see Table 3)
Ceramatec Inc., Salt Lake City/UT	United States	Producer of ceramic materials developing dense mixed ion and electron conducting oxygen (and hydrogen) transport membranes (see Table 3)
Concepts NREC, Inc., White River Junction/VT	United States	Independent turbomachinery design and development company involved in the ITM Oxygen project for IGCC applications (gas turbine integration and precombustor design)
Siemens Power Generation, Inc., Pittsburg/PA	United States	Power generation company involved in the ITM Oxygen project for IGCC applications (gas turbine integration strategy)
SOFCo Holdings, EFS, Alliance/OH (recently acquired by Rolls Royce Fuel Cell Systems)	United States	Company developing ceramic fuel cell components involved in the ITM Oxygen and ITM Syngas projects (mechanical and vessel systems development)
NovelEdgeTechnologies LLC, New Boston/NH	United States	Developer of IGCC power generation processes involved in the ITM Oxygen project for IGCC applications (integration strategy with steam systems)
Eltron Research Inc., Boulder/CO	United States	Company focused on the development of novel inorganic membrane technologies, e.g., hydrogen and oxygen transport membranes and catalytic membrane reactors.

GE Energy, Atlanta/GA	United States	Developer of power generation equipment (gas turbines) involved in the ITM Oxygen project for IGCC applications
Chevron , Richmond/CA	United States	Energy company involved in the ITM Syngas project and in a project on Pd-alloy hydrogen transport membranes with Pall and Oak Ridge National Laboratory
Shell Global Solutions and CRI/Criterion Inc. Houston/TX	United States	Energy company developing Pd-alloy based metal-supported composite membranes for steam reforming
Pall Corp., Esat Hills/NY	United States	Membrane producer developing Pd-alloy based hydrogen selective membranes
Praxair, Inc., Danbury	United States	Gas producing company developing ceramic mixed oxygen ion and electron conducting membranes for oxygen production and syngas generation in membrane reactors (see Table 3)
BOC Group, Inc. (a Member of the Linde Group), Murray Hill/NJ	United States	Gas supplier developing a fluidized-bed membrane reformer for natural gas together with MRT, Vancouver, Canada (see Table 3)
Johnson Matthey Gas Purification Technology, West Chester/PA	United States	Noble metal and catalyst producer develeoing Pd-alloy membrane based hydrogen purification technology, stationary and onboard hydrogen generators (e.g., HotSpot methanol fuel processor)
Idatech LLC, Bend/OR	United States	Company offering a Pd-alloy membrane based fuel processor for hydrogen generation
Power & Energy, Inc. Ivyland/PA	United States	Company offering Pd-alloy membrane based hydrogen separators and membrane reactors
Hy9 Corp., Hopkinton/MA	United States	Company offering Pd-alloy membrane based hydrogen generators
Distributed Energy Systems, Wallingford/CT	United States	Company offering Pd-alloy membrane based hydrogen generators
Wah Chang, Albany/OR	United States	Company offering Pd-alloy based membrane and membrane modules for hydrogen purifcation
REB Research & Consulting, Ferndale/MI.	United States	Company offering metal hydrogen separation membranes and hydrogen generators based on such membranes (methanol reforming)

Green Hydrotec Inc., Kweishan	Taiwan	Small company focused on hydrogen energy technology offering membrane reformers for hydrogen production from methanol solutions

5.2 End users
(Describe the existing and potential end-users, other than those already listed in Table 2)

Potential end users of selective membrane reactors can be found in many industrial sectors, e.g., production of industrial gases, chemical industry, electrical power generation, and water utilities.

6. Expert's brief final judgment on the technology
(maximum 5 sentences)

Selective membrane reactors today have not yet found widespread use in the chemical and process industry, even if membrane bioreactors for water and wastewater treatment and, to some extent, enzyme/chemzyme membrane reactors and pervaporation membrane reactors are applied on industrial scale. The main reasons are the limited availability and high cost of membranes that can withstand the reaction conditions and the high demands on the reactor design (sealing, etc.). The largest potential benefits in terms of cost reduction, compact plant design, efficiency gain, and carbon dioxide capture are certainly being offered by selective membrane reactors for hydrogen production (hydrogen permeable membranes) and for syngas generation (oxygen permeable membranes), e.g., for IGCC power plants, bulk chemicals production, and for (local) provision of fuel cell hydrogen from fossil or regenerative fuels. Although strong industrial development efforts have been underway for more than a decade, these efforts will have to be continued as the challenges in successfully developing these revolutionary technologies remain exceptionally high.